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THE ROYAL INSTITUTE OF CHEMISTRY of Great Britain and Ireland

LECTURES, MONOGRAPHS AND REPORTS, 1957

No. 5

HYDRAZINE

AND ITS DERIVATIVES

EDITED BY

R. A. REED,

B.SC., PH.D., F.R.I.C.

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HYDRAZINE AND ITS DERIVATIVES

By R. A. Reed, B.SC., PH.D., F.R.I.C.

It is the purpose of this monograph to provide an up-to-date account of the chemistry of hydrazine and its main derivatives (other than aryl substitution compounds) and of the uses to which hydrazine may be put. Previous publications on the subject, namely Imbert's *L'Hydrazine et ses dérivés* (Baillière, 1899), Wieland's *Die Hydrazine* (Enke, 1913), Audrieth and Ogg's *The Chemistry of Hydrazine* (Wiley, 1951) and Clark's *Hydrazine* (Mathieson Chemical Corporation, 1953) have dealt with the simple inorganic salts, the co-ordination compounds and the use of anhydrous hydrazine as a solvent—subjects not treated here—as well as the use of hydrazine in organic chemistry. Work on hydrazine derivatives has proceeded sufficiently rapidly during the intervening years to make a new publication, especially one from this country, well overdue. Some duplication of the previous works is however inevitable, since the major consideration has been to show the great versatility of the substance.

In this monograph the practical and arbitrary principle is adopted that hydrazine itself should be the precursor of all starting materials. For this reason the reactions of phenylhydrazine and its homologues, for example, are not included.

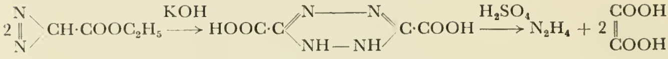
The outstanding names in hydrazine chemistry are undoubtedly Curtius, Thiele, Stollé and Audrieth, and the latter's work in recent years is drawn on quite extensively. For convenience the monograph is divided into four main sections, dealing respectively with the manufacture of hydrazine, the organic chemistry of hydrazine, hydrazine as a reducing agent and industrial applications of hydrazine derivatives.

Some general remarks on the toxic properties of hydrazine, together with a table listing the physical properties of anhydrous and aqueous hydrazine, are given at the end of the first section on page 13.

I. MANUFACTURE OF HYDRAZINE

During the past fifty years hydrazine, N_2H_4, has emerged from an interesting curiosity to a chemical manufactured in tons.

Hydrazine, in the form of its derivatives, the hydrazo-compounds, has been known since 1863, and from 1875 onwards Emil Fischer[1] prepared and characterised the aryl hydrazines. It was not until 1887, however, that Curtius[2,3,4] succeeded in isolating hydrazine itself by the action of alkali on diazoacetic ester:



dihydrotetrazinic acid

Raschig,[5,6,7,8,9] following a suggestion by Thiele,[10] showed that hydrazine could be produced by the action of sodium hypochlorite on aqueous ammonia, the yield being greater in presence of excess ammonia. The mechanism involved the initial formation of chloramine, this being a rapid reaction, followed by the much slower reaction of chloramine with excess ammonia to form hydrazine. Nitrogen is produced as a by-product by the action of chloramine on ammonia, and by the action of chloramine on hydrazine.

$$\begin{aligned} &NH_3 + NaOCl \longrightarrow NH_2Cl + NaOH \\ &NH_2Cl + NH_3 + NaOH \longrightarrow NH_2\text{–}NH_2 + NaCl + H_2O \\ &3NH_2Cl + 2NH_3 \longrightarrow N_2 + 3NH_4Cl \\ &2NH_2Cl + N_2H_4 \longrightarrow N_2 + 2NH_4Cl \end{aligned}$$

The reaction is particularly sensitive to the presence of ions of copper, lead, iron, mercury and especially cobalt.

Raschig found that 60 to 70 per cent yields of hydrazine could be obtained in the presence of glue or gelatin and attributed this effect to the increased viscosity of the solution. It now seems more probable that the effect of glue was to inhibit the catalytic decomposition of chloramine by heavy-metal impurities.

Joyner[11] showed that increasing the ammonia : hypochlorite ratio increased the yield of hydrazine and that the yield was proportional to the amount of glue added when this was present in small amounts. The use of partially hydrolysed glue obviated the foaming troubles obtained when using ordinary glue.[12]

The manufacture of hydrazine by a similar procedure from urea instead of ammonia was patented about this time,[13–17] yields of 70 per cent being obtained.

$$NaOCl + NH_2\text{-}CO\text{-}NH_2 + 2NaOH = N_2H_4 + NaCl + Na_2CO_3 + H_2O$$

The discovery that hydrazine hydrate containing 15 per cent methanol could be employed as a rocket fuel when mixed with oxidising agents such as nitric acid, hydrogen peroxide or oxygen stimulated the expansion of hydrazine production in Germany during the second world war.[18,19]

Two major advances in technology were achieved during this period, the first through the discovery that by rapid heating of the chloramine–ammonia mixtures the reaction producing hydrazine could be accelerated over that producing nitrogen, resulting in increased yields, and the second, that the base could be recovered from the reaction mixture by the use of a conventional salting evaporator and rectification unit.

A pilot plant producing 20 tons per month of hydrazine hydrate was operated at Leverkusen, and a second using the urea route was erected at Ludwigshafen.

A plant consisting of three units each of 100 tons per month capacity was being built at Gersthofen towards the end of the war, of which only one unit operated on a production basis.

The large capacity of the Gersthofen plant enabled certain steam economies to be employed, which would not be practicable on a smaller unit, and for that reason will be described here.

In this process 8 per cent caustic soda solution was chlorinated batchwise in 'Vinidur'-lined steel vessels fitted with a 'Vinidur' sparger and stoneware cooling coils. The resulting hypochlorite, containing 7 per cent available chlorine, was mixed with two volumes of 28·3 per cent w/w ammonia solution in a glass mixing vessel situated on the suction of a three-throw vertical ram pump. Trouble had been experienced by gas locking of this pump, owing to by-product nitrogen accumulating in the valves and cylinders. The mixture of chloramine and ammonia was pumped at 450 p.s.i. through a heat exchanger where its temperature was raised as rapidly as possible to 160–180°C in small-bore stainless tubes, jacketed with 450 p.s.i. steam, the residence time being 1 to 1·3 sec. In this manner the reaction producing hydrazine was accelerated over the side-reactions producing nitrogen, enabling yields of 70 per cent theory to be attained. Two litres of 10 to 20 per cent glue were added hourly to inhibit the effect of heavy-metal impurities. On leaving the reactor, the pressure was reduced to atmospheric, when two-thirds of the excess ammonia and some steam flashed off and were scrubbed with aqueous ammonia in two expansion towers. The combined liquid product from the towers was stripped of the remaining ammonia and some steam in a mild-steel stripping column. The vapour was condensed in a tubular condenser, the condensate being pumped to the head of a second condenser, which acted as a falling film absorber for the ammonia from the two flash towers and make-up ammonia, reconstituting 28 per cent ammonia solution for recycle.

The bottoms from the stripping column containing 3 per cent hydrazine hydrate were freed from salt in a conventional forced circulation salting evaporator constructed of V4A stainless steel. The vapour leaving the salting evaporator was stripped of hydrazine in a column, yielding 15 per cent hydrazine hydrate as a bottoms product. This solution was concentrated to 50 per cent in a packed distillation column with a reflux ratio of 2 : 1 and finally to 95 per cent in a bubble-plate column using a reflux ratio of 6 : 1.

Initially the 95 per cent column was packed with stainless steel turnings, resulting in an explosion that was attributed to the sharp edges of the turnings initiating an explosive reaction of the hydrazine with air drawn in at the condenser vent. Replacement of the turnings with bubble caps and purging with nitrogen gave satisfactory operation. Overall yields of 60 to 70 per cent were obtained.

Dilute solutions and high ammonia : hypochlorite ratios are essential for reasonable yields; hence evaporation costs are high, amounting to one-sixth of the total factory cost of hydrazine.

To reduce this figure, a thermocompressor was used to recompress the steam from the head of the salting evaporator stripping column for use on the reboiler of the ammonia stripping column. Since the available steam pressure from the thermocompressor was only 9 p.s.i., and the boiling point of the bottoms was 103°C, a very large heating surface was necessary. A further attempt to save steam was made by flashing the condensate from the high pressure reactor down to 60 p.s.i.

To purge the system of metallic impurities, steam condensate was used throughout as make-up water and for washing the salt free of hydrazine before disposal.

Various other means of saving steam have been examined by the authors, the following being the most important:

(1) Supplying reflux to the heads of the 50 and 90 per cent rectification columns in the form of condensate and recompressing this steam with that from the salting evaporator stripper, (*a*) by a thermocompressor for use on the ammonia stripper reboiler, or (*b*) by a turbocompressor for use on the salting evaporator callandria. In the latter, however, it has not been possible to locate a turbocompressor with a reasonable efficiency for such a small duty.

(2) The salting evaporator and the two rectifying columns might be run as a triple-effect evaporator by operating the latter *in vacuo*.

(3) By operating the ammonia stripping column under a pressure intermediate between that of the reactor and atmospheric pressure, part of the steam and ammonia may be condensed in the callandria of the salting evaporator, giving up its heat thereto and effecting the evaporation.

FACTORS AFFECTING THE YIELD OF HYDRAZINE

The effects of temperature, ammonia : hypochlorite ratio, residence time and additives on the yield of hydrazine have been investigated by the authors in a dynamic apparatus at temperatures up to 200°C and pressure of 750 p.s.i.

The effect of temperature on the yield of hydrazine for differing ammonia : hypochlorite ratios is shown in Figure 1. In the absence of catalysts, little hydrazine is formed below 60°C, the optimum temperature being 150° to 160°C. The yield increases with increasing ammonia : hypochlorite ratios.

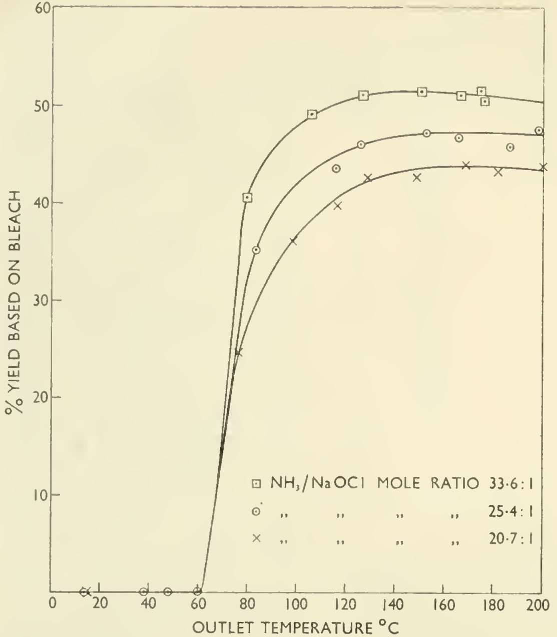


Fig. 1. Relationship between temperature and hydrazine yield for different ammonia/bleach ratios

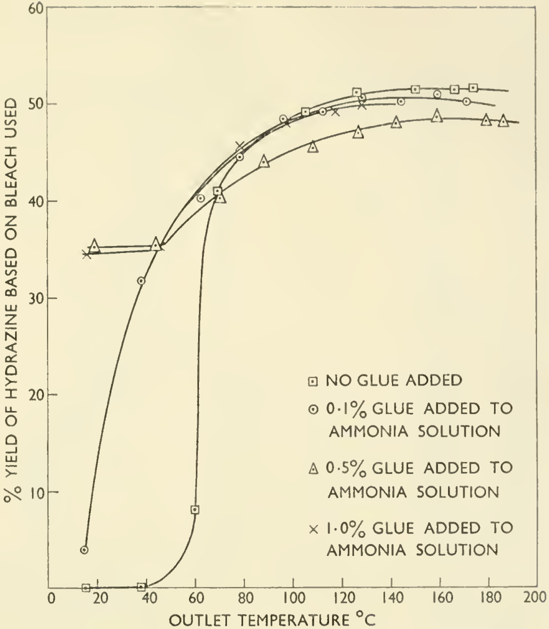


Fig. 2. Effect of increasing amounts of glue on the yield of hydrazine

Figure 2 shows the effect of increasing the amounts of glue, which appears to catalyse the formation of hydrazine even at room temperature. Above 60°C the purely thermal reaction predominates, the final yield being unchanged.

A similar set of curves is shown in Figure 3. Here a constant amount of glue was added, the ammonia : hypochlorite ratio being varied.

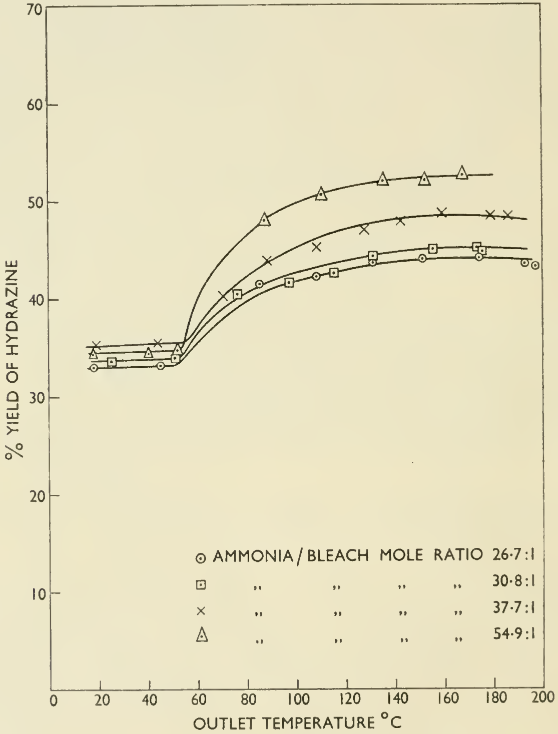


FIG. 3. Effect of temperature on the yield of hydrazine for different ammonia/hypochlorite ratios in presence of glue (0·5%)

The effect of residence time is shown in Figure 4. Decreasing the residence time from 8·4 to 2·7 sec increases the yield only slightly. The runs in the two upper curves were carried out in the presence of ethylenediamine tetra-acetic acid and, in the case of the lower curve, no additive was present. It is evident that removal of the heavy metal ions results in increased yield. Using E.D.T.A. the yield-of-hydrazine/temperature curves are similar to those for the uncatalysed reaction, little hydrazine being formed below 60°C. This seems to indicate that

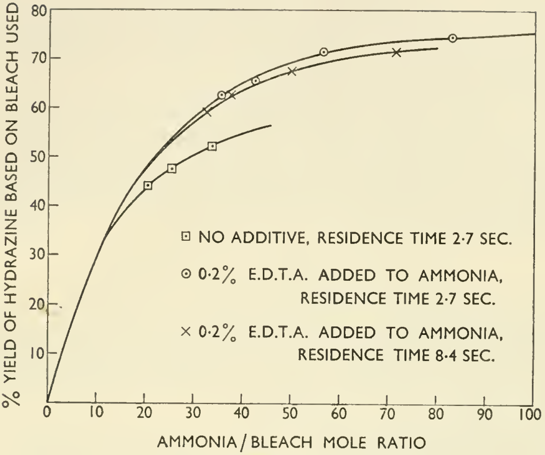


FIG. 4. Effect of increased residence time and addition of E.D.T.A. on the yield of hydrazine

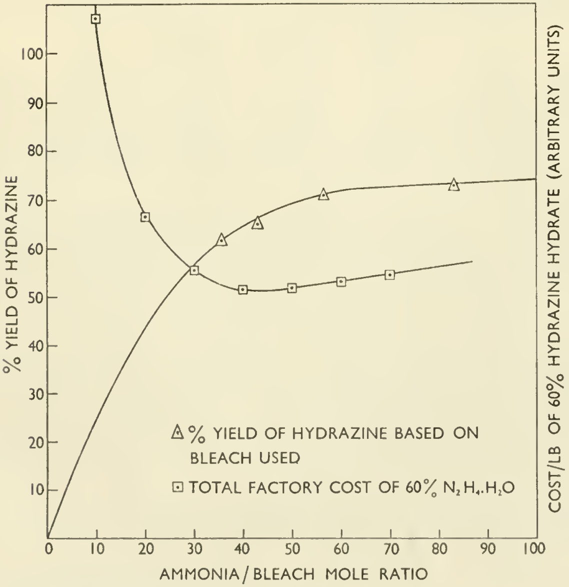


FIG. 5. Relationship between ammonia/bleach ratio and the yield and cost of hydrazine

glue acts as a positive catalyst for the production of hydrazine, whereas E.D.T.A. acts by removal of the metal ions that would otherwise catalyse the decomposition of chloramine.

The effect of change in the ammonia : hypochlorite ratios is shown in Figure 5. High ratios result in increased yields, but also in high evaporation costs; lower ratios give poorer yields but lower steam charges. Heat and material balances have been calculated and the total factory cost determined for various ammonia : hypochlorite ratios. The cost curve exhibits a minimum cost for an ammonia : hypochlorite ratio of 44, the yield of hydrazine at that point being 67 per cent.

USE OF ANHYDROUS AMMONIA

Sisler and co-workers[20,21,22] in the U.S.A. have examined the direct chlorination of anhydrous ammonia as a possible means of reducing steam costs. With chlorine in carbon tetrachloride, and an NH_3 to Cl_2 ratio of 120 : 1, the maximum yield of hydrazine was 10·4 per cent. Chlorine diluted with nitrogen and an NH_3 to Cl_2 ratio of 267 : 1 gave a maximum yield of 30·6 per cent.

By introducing chlorine into a stream of ammonia through a spinneret, with an NH_3 to Cl_2 ratio of 32·8 : 1, yields of chloramine as high as 94 per cent were obtained, and the apparatus could be run for long periods without clogging the jet with by-product ammonium chloride.

$$2NH_3 + Cl_2 = NH_2Cl + NH_4Cl$$
$$NH_2Cl + 2NH_3 = N_2H_4 + NH_4Cl$$

Filtering out the ammonium chloride through glass wool and absorbing the chloramine in liquid ammonia such that the final NH_3 mole ratio was 365 : 1 gave yields of hydrazine of 32·7 per cent.

Considering the large excess of ammonia necessary it would appear that the above process holds little advantage over the modified Raschig process.

A further variation of this process is disclosed in Canadian Patents 523,484 and 523,485, where hydrazine is produced by the reaction of ammonia and chlorine in the presence of activated alumina.

ALTERNATIVE SYNTHESES OF HYDRAZINE

Since further improvement in the Raschig process can only produce a marginal lowering of costs, a great deal of effort, especially in the U.S.A., has been put into the search for a cheap synthetic route.

Raw material costs alone rule out many possible routes, for to compete with the Raschig process the raw material costs must be low and the process reasonably direct.

In the absence of experimental data it has proved convenient to screen proposed routes on a thermodynamic basis.

If the standard free energy for the reaction be calculated,

then $\Delta F^\circ = -RT \log K_a$,

$$\text{where } K_a = \text{Equilibrium constant} = \frac{\text{Activities of the products}}{\text{Activities of the reactants}}$$

The following criteria of Dodge[23] may be employed as a rough guide to the feasibility of a reaction.

If $\Delta F^\circ < 0$, the reaction is promising.

If $\Delta F^\circ > 0$ but $< 10{,}000$, reaction is of doubtful promise but warrants further study.

If $\Delta F^\circ > 10{,}000$, reaction is very unfavourable and would be feasible only in special circumstances.

The possible routes may be divided according to the following classification :

SYNTHESIS FROM THE ELEMENTS

$$N_2 + 2H_2 \longrightarrow N_2H_4$$

The values of the free energy and equilibrium constant have been calculated for various temperatures and compared with the data of Scott[24] in Table I.

TABLE I

Temp °K	$F_{(g)}$ cal/mole		$\log_{10}K$	
	Calc.	Scott	Calc.	Scott
298·1	37,855	37,890	−27·76	−27·77
400	43,120	43,180	−23·57	−23·59
500	48,477	48,520	−21·19	−21·21
600	53,587	53,960	−19·51	−19·65
700	59,351	59,440	−18·53	−18·56
800	65,081	64,950	−17·78	−17·74
900	70,642	70,470	−17·16	−17·14
1,000	76,354	76,000	−16·69	−16·61

The competing reaction is $\frac{1}{2}N_2 + \frac{3}{2}H_2 = NH_3$, for which $\Delta F^\circ_{(g)}$ at $298\cdot1\,^\circ\mathrm{K} = -3976$ cal/mole and $\log_{10}K = 2\cdot918$.[25]

It is evident that the free energy of formation is very unfavourable for hydrazine formation, but much more favourable for ammonia production. Pressure would assist both reactions, but the effect would be greater in the case of ammonia formation.

Gedye and Rideal[26] obtained a 4 per cent yield of hydrazine by passing nitrogen and hydrogen over a promoted iron catalyst at 437°C, the conversion per pass, however, being only 1 per cent of this value.

Only traces of hydrazine have been obtained by subjecting mixtures of nitrogen and hydrogen to mercury-sensitised photolysis,[27] the action of cathode rays[28] or to an electric discharge.[29]

OXIDATION OF AMMONIA BY AGENTS OTHER THAN HYPOCHLORITE

Direct oxidation with gaseous oxygen :

$$2NH_{3(g)} + \tfrac{1}{2}O_{2(g)} = N_2H_{4(g)} + H_2O_{(g)} \qquad \ldots \quad \ldots \qquad (1)$$

$$\Delta F^\circ_{298\cdot1(g)} = -8728 \text{ cal/mole}$$

Competing reaction:

$$2NH_{3(g)} + \tfrac{3}{2}O_{2(g)} = N_{2(g)} + 3H_2O_{(g)} \quad \ldots \quad \ldots \quad \ldots \quad (2)$$
$$\Delta F^\circ_{298\cdot1(g)} = -155{,}953 \text{ cal/mole}$$

Reaction (1) is thermodynamically feasible, but reaction (2) is much more favourable. To obtain satisfactory yields of hydrazine, a catalyst must be sought to promote (1) or inhibit (2). Pressure would assist (1) but would have little effect on (2), since this is accompanied by an increase in volume.

Raschig[30,31] found traces of hydrazine on rapidly quenching an ammonia–oxygen flame.

Pattison[32] obtained 0·04 per cent hydrazine by quenching at 0°C and 0·12 to 0·14 per cent by quenching on a wall cooled by solid carbon dioxide and trichloroethylene. Submerged combustion was also tried with little success.

Oxidation of ammonia by nitrous oxide:

$$N_2O_{(g)} + 2NH_{3(g)} = N_2H_{4(g)} + H_2O_{(g)} + N_{2(g)} \quad \ldots \quad (3)$$
$$\Delta F^\circ_{298\cdot1} = -33{,}483 \text{ cal/mole}$$

Competing reactions:

$$N_2O_{(g)} + 6NH_{3(g)} = 4N_2H_{4(g)} + H_2O_{(g)} \quad \ldots \quad \ldots \quad (4)$$
$$\Delta F^\circ_{298\cdot1} = 96{,}301 \text{ cal/mole}$$

$$3N_2O_{(g)} + 2NH_{3(g)} = 4N_{2(g)} + 3H_2O_{(g)} \quad \ldots \quad \ldots \quad (5)$$
$$\Delta F^\circ_{298\cdot1} = -230{,}233 \text{ cal/mole}$$

Reaction (5) yielding nitrogen is far more probable than (3) producing hydrazine, whereas (4) is highly improbable.

Pattison and co-workers[32] of the Battelle Institute have calculated the ultimate composition of the product, assuming that all reactions attain equilibrium, and have shown that only a trace of hydrazine would be present. Here again a catalyst must be sought to promote reaction (3) or inhibit (5). The same authors found that the yield of hydrazine, based on the amount of nitrous oxide fed, was around 0·1 per cent. Patry[33] obtained similar results, whilst Mantell and Passino[34] claimed high yields with nickel on kieselguhr or reduced cobalt oxide on alumina. No actual yields were quoted, however.

Oxidation of ammonia by silver oxide:

$$2NH_{3(g)} + Ag_2O_{(s)} = N_2H_{4(g)} + 2Ag + H_2O \quad \ldots \quad (6)$$
$$\Delta F^\circ_{298\cdot1} = -6{,}068 \text{ cal/mole}$$

Competing reaction:

$$2NH_{3(g)} + 3Ag_2O_{(s)} = N_{2(g)} + 3H_2O_{(g)} + 6Ag_{(s)} \quad \ldots \quad (7)$$
$$\Delta F^\circ_{298\cdot1} = -148{,}768 \text{ cal/mole}$$

Reaction (6) is thermodynamically feasible but (7) is much more probable. Since silver oxide has the lowest free energy of formation of the metallic oxides, the free energy for the reaction will be the most negative in (6) and conditions for hydrazine production most favourable.

Oxidation of ammonia by silver oxide in a conventional fluidised bed system has been described,[35] and also a fixed bed system with the oxides or metals of the group Ag, Cu, Zn, Sn, Pb or Cd.[36] No yields are given for either system, however.

REDUCTION OF NITROUS OXIDE BY HYDROGEN

$$N_2O_{(g)} + 3H_{2(g)} = N_2H_{4(g)} + H_2O_{(g)} \quad \ldots \quad \ldots \quad (8)$$
$$\Delta F^\circ_{298 \cdot 1} = -41{,}435 \text{ cal/mole}$$

Competing reactions are:

$$N_2O_{(g)} + H_{2(g)} = N_{2(g)} + H_2O_{(g)} \quad \ldots \quad \ldots \quad \ldots \quad (9)$$
$$\Delta F^\circ_{298 \cdot 1} = -79{,}395 \text{ cal/mole}$$

$$N_2O_{(g)} + 4H_{2(g)} = 2NH_{3(g)} + H_2O_{(g)} \quad \ldots \quad \ldots \quad \ldots \quad (10)$$
$$\Delta F^\circ_{298 \cdot 1} = -87{,}347 \text{ cal/mole}$$

It is evident that conditions for both competing reactions are more favourable than for that producing hydrazine. Increased pressure would assist (8) and to a less extent (10), since both are accompanied by a decrease in volume.

Mantell and Passino[37] have claimed high yields for reduction of nitrous oxide by hydrogen with a reduced iron catalyst at temperatures of 21–480°C with a contact time of 0·72 sec.

DECOMPOSITION OF UREA IN THE PRESENCE OF CARBONYL-FORMING METALS

The manufacture of hydrazine by reaction of urea with nickel or iron has been described.[38,39] Temperatures of 132–150°C are used with iron, but much lower temperatures around 60–70°C may be employed with nickel.

The overall reaction is not very favourable:

$$CO(NH_2)_{2(s)} \longrightarrow CO + N_2H_{4(g)}$$
$$\Delta F^\circ_{298 \cdot 1} = 74{,}785 \text{ cal/mole}$$

The reaction postulating the intermediate formation of nickel or iron carbonyls may be much more favourable, since

$$\Delta H_f \;\; Fe(CO)_{5(g)} = 180{,}000 \text{ cal/mole}$$

The free energy of formation is not known, however, so that the equilibrium constants cannot be evaluated.

PRODUCTION OF HYDRAZINE BY ELECTRIC DISCHARGE THROUGH AMMONIA

The decomposition of ammonia by means of an electric discharge gives good yields of hydrazine based on the ammonia decomposed; the yield per pass, however, is very low. The current efficiency, although improved by coating the cell walls with platinum to promote recombination of the hydrogen atoms, is still quite low (*see* Table II).

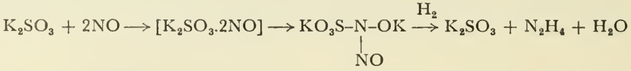
Gunning and co-workers[43,44] have investigated the photolysis of ammonia with light of wave-length 1849Å and also by mercury-sensitised photolysis at 2537Å. Yields as high as 89 per cent were obtained, but the conversion per pass was again very low.

TABLE II

Authors	Percentage yield of hydrazine based on NH_3 decomp.	Percentage yield of hydrazine per pass	Grams N_2H_4/kWh	
Koenig & Wagner [40]	46·5	0·0296	2·28	
	54·2	0·0296	2·35	
	60·6	0·0156	3·92	
	80·4	0·012	3·15	
Ouchi [41]		0·014	42·7	
		0·0145	46·1	
		0·0142	47·0	
Devins & Burton [42]	91	0·033	30	Walls platinum coated
	92	0·094	43	
	85	0·022	23	

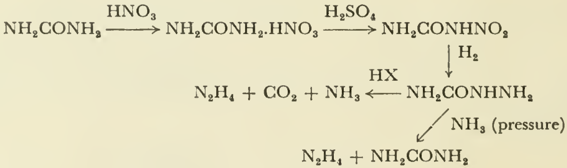
Two other methods of potential interest for the manufacture of hydrazine are:

(i)



$$K_2SO_3 + 2NO \longrightarrow [K_2SO_3.2NO] \longrightarrow KO_3S\text{-}\underset{\substack{| \\ NO}}{N}\text{-}OK \xrightarrow{H_2} K_2SO_3 + N_2H_4 + H_2O$$

(ii)[113]



$$\begin{tikzcd}
NH_2CONH_2 \arrow[r, "HNO_3"] & NH_2CONH_2.HNO_3 \arrow[r, "H_2SO_4"] & NH_2CONHNO_2 \arrow[d, "H_2"] \\
& N_2H_4 + CO_2 + NH_3 & NH_2CONHNH_2 \arrow[l, "HX"'] \arrow[dl, "NH_3\ \text{(pressure)}"] \\
& N_2H_4 + NH_2CONH_2 &
\end{tikzcd}$$

ANHYDROUS HYDRAZINE

Anhydrous hydrazine is produced chiefly by one of two methods.

(*a*) Aqueous hydrazine is distilled in the presence of sufficient NaOH to give a molar ratio $NaOH:H_2O$ of at least one. This operation is attended by considerable hazard, since boiling anhydrous hydrazine is a very sensitive material and explosions have been recorded. Operation under vacuum with a blanket of nitrogen is the least precaution that should be taken.

A recent patent of Olin Mathieson[45] claims that the explosion risk may be removed entirely even at atmospheric pressure by distilling aqueous hydrazine and NaOH in the presence of a saturated aliphatic hydrocarbon of boiling point between 90° and 150°C. Thus in an example given by Mathieson, a mixture of 500 parts by weight of 54·5 per cent N_2H_4, 523 parts 97 per cent NaOH and 200 parts of a petroleum cut (b.p. 121° to 143°C) is distilled at atmospheric pressure, the fraction boiling at 103·5° to 107°C collected and the non-organic layer separated from the distillate. The yield is 99 per cent of the theoretical, the hydrazine being 96·3 per cent N_2H_4.

(*b*) Solid hydrazine sulphate is treated with excess liquid ammonia and filtered from ammonium sulphate. Anhydrous hydrazine remains after evaporation of the excess ammonia.[46]

$$N_2H_4.H_2SO_4 + 2NH_3 \longrightarrow N_2H_4 + (NH_4)_2SO_4$$

TOXICITY OF HYDRAZINE

Exposure to the vapour of strong hydrazine solutions leads to a delayed eye irritation which later passes off. Inhalation of such vapour produces an attack upon the nose and throat. It should be emphasised that the manufacture of hydrazine calls for a well-ventilated factory, since recent experiments have shown that the concentration of hydrazine in the atmosphere should not exceed 6 mg/m³. Three times this concentration was fatal to the animals used in the experiments. Similar animals responded, however, to treatment with sodium pyruvate or α-ketoglutarate, providing the treatment was used within half an hour of exposure.[47]

Spillage on the skin should be treated as for caustic soda. Isolated cases of dermatitis have been reported, but only one case of dermatitis has been encountered at Loughborough during sixteen years of manufacture and use.

The physical properties of hydrazine are given in Table III.

TABLE III

PHYSICAL PROPERTIES OF HYDRAZINE

	100 per cent	64 per cent
Boiling point	113·5°C	119·5°C
Freezing point	2·0°C	−51·7°C
Flash point (open cup)	125°F	160°F
Density	1·008 (20°C)	1·032 (25°C)
Viscosity at 20°C	0·97cP	1·2cP
Surface tension at 25°C (dyne/cm) ..	66·7	74·3
n_D^{22}	1·470	1·430
Dielectric constant at 20°C	53	—

It should be noted that 64 per cent hydrazine is equivalent to 100 per cent hydrazine hydrate

II. ORGANIC CHEMISTRY OF HYDRAZINE

Hydrazine is the simplest possible diamine, and as such is a very reactive substance, leading to both open-chain compounds and ring systems. Open-chain compounds that can be obtained from hydrazine hydrate will be considered first.

HYDRAZIDES

The formation of hydrazides may be represented most simply by the following equations :

$$R{\cdot}CO{\cdot}X + NH_2{\cdot}NH_2 \longrightarrow R{\cdot}CO{\cdot}NH{\cdot}NH_2 + HX \quad .. \quad .. \quad (1)$$

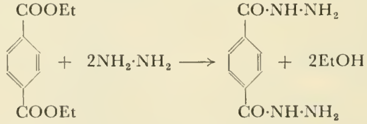
$$2R{\cdot}CO{\cdot}X + NH_2{\cdot}NH_2 \longrightarrow R{\cdot}CO{\cdot}NH{\cdot}NH{\cdot}CO{\cdot}R + 2HX \quad .. \quad (2)$$

where the compound RCO·X may represent an acid halide, an ester, an amide or an acid anhydride, the amount used determining whether reaction (1) or (2) takes place predominantly.

With acid halides, an acid acceptor such as NaOH, Na_2CO_3, pyridine or NH_3 should be employed, the last indicating that the rate of reaction with hydrazine exceeds that with ammonia. The group R can represent alkyl or aryl, and reaction occurs in cold aqueous solution.

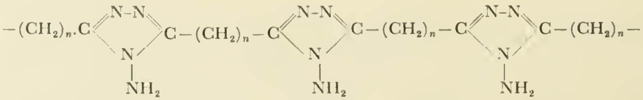
Reactions with esters and amides, on the other hand, need reflux conditions; alcohol may be required as a solvent, although this can usually be avoided by slow addition of the ester or amide to hydrazine solutions of 38 to 64 per cent strength.

Polyesters, such as terephthalic ester, generally give polyhydrazides.



Cyclic hydrazides are obtained with *o*-diesters. These are discussed later under ring systems.

Whereas the higher (*e.g.* stearic) hydrazides may be made by co-distilling water from a solution of hydrazine stearate with toluene, the dibasic acids, *e.g.* maleic, succinic and adipic acids, give water-soluble polymers, which may be cyclised on heating to amino-triazol polymers.

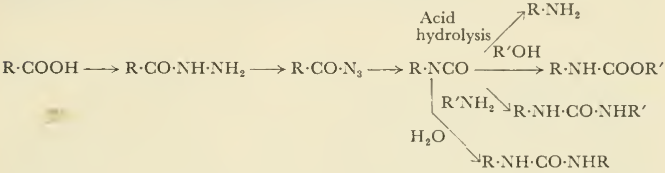


Hydrazides are solid compounds, the lower alkyl derivatives having low melting points and being soluble in water. The higher alkyl and the aryl derivatives are insoluble in water; the latter are soluble in NaOH, the –CONHNH– grouping here being acidic, as it is also in the diacylhydrazines, RCONHNHCOR.

Primary hydrazides, $RCONHNH_2$, retain the reducing power of hydrazine towards both Fehling's solution and ammoniacal silver nitrate. They react with carbonyl groups similarly to phenylhydrazine, *e.g.*

$$RCONHNH_2 + R^1COR^2 \longrightarrow RCONHN{=}CR^1R^2$$

Reaction of any primary hydrazide with nitrous acid yields the corresponding acid azide, which on heating in an inert solvent readily decomposes with rearrangement to give the isocyanate. The isocyanate may in turn be converted to an amine, a urethane or a urea.



A further very important synthetic use for hydrazides since 1936 bears the name of the McFadyen-Stevens reaction, in which a benzenesulphonylhydrazide is heated with Na_2CO_3 in aqueous or glycol solution, the product being an aldehyde.[48]

$$R{\cdot}CO{\cdot}NH{\cdot}NH_2 \xrightarrow{Ph{\cdot}SO_2Cl} R{\cdot}CO{\cdot}NH{\cdot}NH{\cdot}SO_2Ph \longrightarrow R{\cdot}CHO$$

This reaction occurs only with the aromatic series.

HYDRAZONES AND AZINES

Carbonyl compounds may theoretically react with one or both amino groups of hydrazine, as follows:

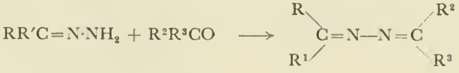
$$R{\cdot}CO{\cdot}R' + NH_2NH_2 \longrightarrow \underset{\text{Hydrazone}}{RR'C{=}N{\cdot}NH_2}$$

$$2\,R{\cdot}CO{\cdot}R' + NH_2NH_2 \longrightarrow \underset{\text{Azine}}{RR'C{=}N{-}N{=}CRR'}$$

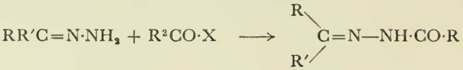
Aldehydes react more quickly than ketones. In fact aldehyde hydrazones react with a second molecule of aldehyde more rapidly than with hydrazine itself so that the aldazine is the normal product. Ketazines, on the other hand, require the presence of an excess of ketone together with acetic or formic acid as catalyst.[49]

Benzalazine may be made simply by shaking benzaldehyde with a dilute aqueous solution of hydrazine at room temperature. On heating with dilute mineral acids, hydrazones and azines are hydrolysed to give hydrazine salts and the original carbonyl compound, both recoveries being excellent.[50]

Aliphatic hydrazones are strongly basic, and the aromatic weakly basic; both can condense with a new carbonyl compound to form mixed azines.



With an acyl compound they give acyl hydrazones.



$$RR'C{=}N{\cdot}NH_2 + R^2CO{\cdot}X \longrightarrow \underset{R'}{\overset{R}{}}\!\!>C{=}N{-}NH{\cdot}CO{\cdot}R$$

It is sometimes required to exchange the group =N—N= for an azo group (—N=N—), and this may be done by reducing an azine catalytically over palladium or platinum at 50 lb/in² pressure to give the hydrazo-compound, which is readily oxidisable to the required azohydrocarbon with cupric salts,[51] potassium chromate,[190] oxygen[192] or hydrogen peroxide.[193]

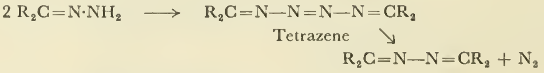
$$R_2C{=}N{-}N{=}CR_2 \xrightarrow{H_2} R_2CH{\cdot}NH{\cdot}NH{\cdot}CHR_2 \xrightarrow{O_2} R_2CH{-}N{=}N{-}CHR_2$$

The resulting azo compounds form free radicals, which may be used to initiate polymerisation reactions.

The azo group in aliphatic compounds is notoriously labile and is usually lost as nitrogen on heating.

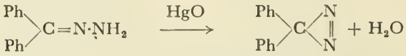
When Raney nickel is used as catalyst, the reduction proceeds beyond the hydrazo stage to give the corresponding amine.[52] Azines of certain carbonyl compounds, like 3-methyl-5-alkyl-2-*cyclo*hexen-1-ones and the alkylated 1-tetralones, are aromatised to the corresponding 3-methyl-5-alkylanilines and 1-aminonaphthalenes by boiling with a palladium–carbon catalyst in triethylbenzene.[53]

Oxidation of aliphatic hydrazones by iodine usually leads to tetrazenes, which have a tendency to lose nitrogen and pass to the corresponding azine.

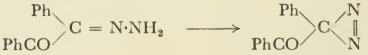


$$2\,R_2C{=}N{\cdot}NH_2 \longrightarrow \underset{\text{Tetrazene}}{R_2C{=}N{-}N{=}N{-}N{=}CR_2} \searrow R_2C{=}N{-}N{=}CR_2 + N_2$$

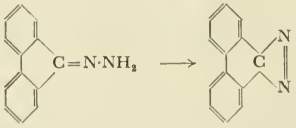
Aromatic hydrazones, on oxidation with mercuric oxide, give diazo compounds in excellent yields.[54]



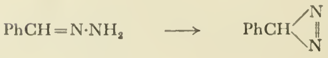
Diphenyldiazomethane



Phenylbenzoyldiazomethane[55]

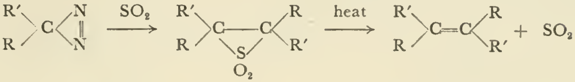


Diazofluorene

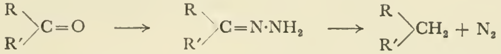


Phenyldiazomethane

With sulphur dioxide these diazo compounds yield sulphones, which decompose on heating to liberate SO_2, forming olefins.[223,224]



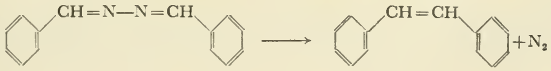
Hydrazones, aliphatic or aromatic, can be degraded by heating with alkalis; this is known as the Kishner-Wolff reaction and is extensively used to reduce carbonyl compounds to hydrocarbons.

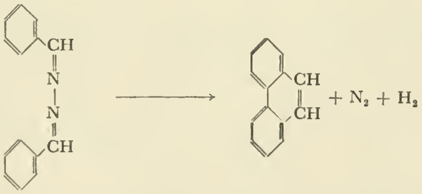


$$\begin{matrix}R\\R'\end{matrix}\!\!>C=O \longrightarrow \begin{matrix}R\\R'\end{matrix}\!\!>C=N\cdot NH_2 \longrightarrow \begin{matrix}R\\R'\end{matrix}\!\!>CH_2 + N_2$$

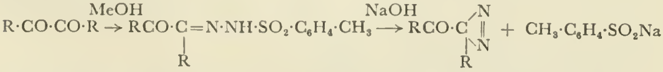
In 1946 Huang-Minlon greatly improved the technique of the reaction, the carbonyl compound being refluxed with 85 per cent hydrazine hydrate and caustic potash in diethylene glycol to form the hydrazone. The reflux is removed and water is distilled off until the temperature reaches 200°C, when the reflux is replaced for three to four hours of further heating.[56] As the yields are very good, this method of reduction is superseding that of Clemmensen, in which amalgamated zinc and acid are used.

Aryl azines are degraded much less readily. Thus, on heating at *ca* 300°C nitrogen is evolved, with the formation of a stilbene derivative. Aryl azines with free *o*-positions are stated to yield phenanthrenes.[57]



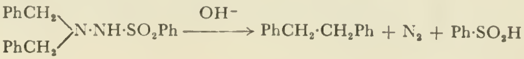


A recent paper[81] describes the preparation of α-diazoketones from α-diketones by treatment with *p*-toluene sulphonhydrazide, followed by NaOH.



$$R\cdot CO\cdot CO\cdot R \xrightarrow{MeOH} RCO\cdot\underset{\displaystyle R}{\underset{|}{C}}=N\cdot NH\cdot SO_2\cdot C_6H_4\cdot CH_3 \xrightarrow{NaOH} RCO\cdot\underset{\displaystyle R}{C}\!\!\begin{matrix}N\\ \|\\ N\end{matrix} + CH_3\cdot C_6H_4\cdot SO_2Na$$

A rather different type of degradation of a sulphonhydrazide has been reported very recently.[194]

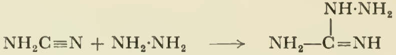


$$\begin{matrix}PhCH_2\\PhCH_2\end{matrix}\!\!>N\cdot NH\cdot SO_2Ph \xrightarrow{OH^-} PhCH_2\cdot CH_2Ph + N_2 + Ph\cdot SO_2H$$

GUANIDINE DERIVATIVES

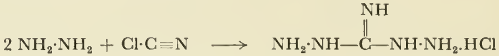
Hydrazine adds to the triple bond of a cyanide or nitrile group, producing guanyl compounds.

Thus, reaction of free cyanamide with aqueous hydrazine[58] gives a solution of aminoguanidine, a valuable intermediate for dyestuffs used in colour photography.



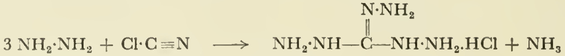
$$NH_2C{\equiv}N + NH_2{\cdot}NH_2 \longrightarrow NH_2{-}\overset{\overset{NH{\cdot}NH_2}{|}}{C}{=}NH$$

With cyanogen chloride two products are possible, depending on the ratio of the two reactants and the solvent used. When two moles of $N_2H_4.H_2O$ are used in a brine solvent, diamino-guanidine hydrochloride is obtained in 70 per cent yield.[59]



$$2\,NH_2{\cdot}NH_2 + Cl{\cdot}C{\equiv}N \longrightarrow NH_2{\cdot}NH{-}\overset{\overset{NH}{\|}}{C}{-}NH{\cdot}NH_2.HCl$$

With three moles $N_2H_4.H_2O$ in water as solvent a 67 per cent yield of triaminoguanidine hydrochloride is obtained.[60]



$$3\,NH_2{\cdot}NH_2 + Cl{\cdot}C{\equiv}N \longrightarrow NH_2{\cdot}NH{-}\overset{\overset{N{\cdot}NH_2}{\|}}{C}{-}NH{\cdot}NH_2.HCl + NH_3$$

ALKYLATION OF HYDRAZINE

Direct alkylation of a substituted hydrazine always occurs at the more basic nitrogen. A consequence of this is that it is difficult to obtain monosubstituted hydrazines, since the alkyl group confers increased basicity on its nitrogen atom and thereby induces asymmetric disubstitution. By contrast, any substituent reducing the basicity, *e.g.* an acetyl group, induces symmetrical disubstitution.

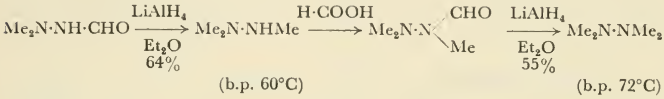
$$RX + N_2H_4 \longrightarrow RNHNH_2 \xrightarrow{RX} R_2NNH_2 \xrightarrow{RX} R_3\overset{+}{N}NH_2 \quad (X{=}Hal.)$$

$$(CH_3CO)_2O + N_2H_4 \longrightarrow [CH_3CO{\cdot}NH{\cdot}NH_2] \xrightarrow{(CH_3CO)_2O} CH_3CO{\cdot}NH{\cdot}NH{\cdot}COCH_3$$

Methyl hydrazine is therefore generally prepared by the indirect method, benzalazine reacting with methyl sulphate in benzene solution, this being followed by hydrolysis.[196] The obstacle of disubstitution can be largely overcome with the higher alkyl groups by refluxing the alkyl bromide with strong hydrazine hydrate in alcoholic solution for many hours and isolating as the acid sulphate.[76]

Symmetrical dimethylation can best be achieved by complete reaction of methyl sulphate with dibenzoylhydrazine followed by hydrolysis.[197] In spite of the ease of asymmetric dialkylation mentioned above, *NN*-dimethylhydrazine is obtained commercially either by the action of chloramine on dimethylamine (Raschig reaction) or by reduction of dimethylnitrosamine.[198,199]

To complete the methyl substituted series, mention must be made of trimethyl hydrazine, which has been synthesised by reduction of formyl *NN*-dimethyl hydrazine and tetramethyl hydrazine by the similar reduction of formyl trimethylhydrazine.[200]



$$Me_2N{\cdot}NH{\cdot}CHO \xrightarrow[\substack{Et_2O \\ 64\%}]{LiAlH_4} \underset{\text{(b.p. 60°C)}}{Me_2N{\cdot}NHMe} \xrightarrow{H{\cdot}COOH} Me_2N{\cdot}N\begin{smallmatrix} CHO \\ Me \end{smallmatrix} \xrightarrow[\substack{Et_2O \\ 55\%}]{LiAlH_4} \underset{\text{(b.p. 72°C)}}{Me_2N{\cdot}NMe_2}$$

MISCELLANEOUS REACTIONS

Hydrazine reacts very readily with ethyl carbonate to give ethyl hydrazine carboxylate (ethyl carbazate), the use of which is commented upon later in connection with ring formation.[61] The percentages given below the arrows are the actual compared with the theoretical yields.

$$NH_2NH_2 + EtO{\cdot}COOEt \xrightarrow[90\%]{} NH_2{\cdot}NH{\cdot}COOEt + EtOH$$

Ethyl chloroformate reacts to give the diester, ethyl hydrazodicarboxylate, a compound that is remarkably stable in conditions that normally lead to hydrolysis, ammonolysis or hydrazinolysis.[62]

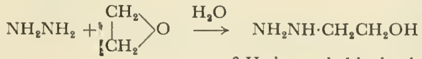
$$NH_2{\cdot}NH_2 + 2\ Cl{\cdot}COOEt \xrightarrow[85\%]{} EtO{\cdot}CO{\cdot}NH{\cdot}NH{\cdot}COOEt + 2\ HCl$$

This ester may be oxidised by chlorine to ethyl azodicarboxylate, better left undistilled.[62]

$$EtO{\cdot}CO{\cdot}NH{\cdot}NH{\cdot}COOEt + Cl_2 \xrightarrow[82\%]{} EtOCO.N{=}N.COOEt + 2\ HCl$$

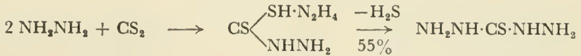
The azo ester undergoes Diels-Alder reactions with great readiness, as described later.

A variety of commercially useful reactions involving hydrazine are represented schematically below, in equations (*a*) to (*o*).

(*a*) 

$$NH_2NH_2 + \begin{smallmatrix} CH_2 \\ | \\ CH_2 \end{smallmatrix}\!\!>\!O \xrightarrow{H_2O} NH_2NH{\cdot}CH_2CH_2OH$$

β-Hydroxyethyl hydrazine[63]

(*b*) 

$$2\ NH_2NH_2 + CS_2 \longrightarrow CS\begin{smallmatrix} SH{\cdot}N_2H_4 \\ NHNH_2 \end{smallmatrix} \xrightarrow[55\%]{-H_2S} NH_2NH{\cdot}CS{\cdot}NHNH_2$$

Thiocarbazide[64]

(*c*) $2\ NH_2NH_2 + COCl_2 \longrightarrow NH_2NH{\cdot}CO{\cdot}NHNH_2 + 2\ HCl$

Carbazide[65]

(*d*) $NH_2NH_2 + C_4H_9ONO + NaOH \xrightarrow[80\%]{EtOH} NaN_3 + C_4H_9OH + 2\ H_2O$

Sodium azide[66]

(*e*) $NH_2NH_2 + NH_2CO{\cdot}NH_2 \xrightarrow[90\%]{Reflux} NH_2NH{\cdot}CO{\cdot}NH_2 + NH_3$

Semicarbazide[67]

(*f*) $NH_2NH_2 + NH_4SCN \xrightarrow[81\%]{\text{Heat}} NH_2NH{\cdot}CS{\cdot}NH_2 + NH_3$

Thiosemicarbazide[68]

(*g*) $NH_2NH_2 + 2\,NaCNO + H_2SO_4 \xrightarrow[95\%]{H_2O} NH_2CO{\cdot}NH{\cdot}NH{\cdot}CO{\cdot}NH_2 + Na_2SO_4$

Biurea[69]

$NH_2NH_2 + 2\,NH_2CO{\cdot}NH_2 \xrightarrow[98\%]{H_2SO_4} NH_2CO{\cdot}NH{\cdot}NH{\cdot}CO{\cdot}NH_2 + 2\,NH_3$ (Ref. 119)

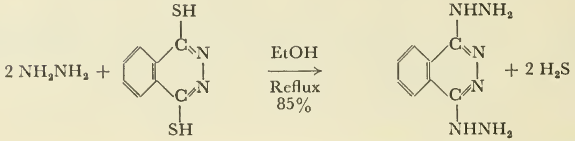
(*h*) $NH_2NH_2 + RSO_2Cl \xrightarrow{NaOH} RSO_2NHNH_2 \xrightarrow{HONO} RSO_2N_3$

Sulphonhydrazide[70] Sulphonazide[71]

(*j*) $NH_2NH_2 + 2\,HCHO + 2\,NaHSO_3 \xrightarrow{H_2O} NaO_2SO{\cdot}CH_2{\cdot}NH{\cdot}NH{\cdot}CH_2{\cdot}OSO_2Na$

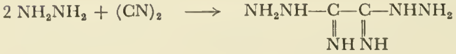
Hydrazomethane sulphonate[72]

(*k*)



1 : 4-Dihydrazinophthalazine[73]

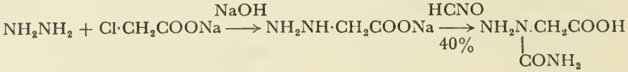
(*l*)



$2\,NH_2NH_2 + (CN)_2 \longrightarrow NH_2NH{-}\underset{\underset{\displaystyle NH}{\|}}{C}{-}\underset{\underset{\displaystyle NH}{\|}}{C}{-}NHNH_2$

Oxalic bis-hydrazidine[74]

(*m*)



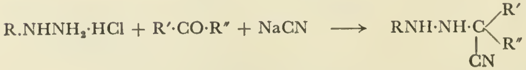
$NH_2NH_2 + Cl{\cdot}CH_2COONa \xrightarrow{NaOH} NH_2NH{\cdot}CH_2COONa \xrightarrow[40\%]{HCNO} NH_2\underset{\underset{\displaystyle CONH_2}{|}}{N}.CH_2COOH$

Semicarbazidoacetic acid[75]

(*n*) $NH_2NH_2 + R.Br \xrightarrow[H_2SO_4]{EtOH} RNHNH_2.H_2SO_4 + HBr$

Alkyl hydrazine sulphate[76]

(*o*)



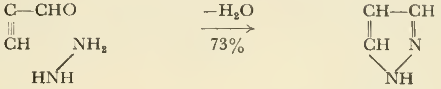
$R.NHNH_2{\cdot}HCl + R'{\cdot}CO{\cdot}R'' + NaCN \longrightarrow RNH{\cdot}NH{\cdot}\underset{\underset{\displaystyle CN}{|}}{C}\begin{smallmatrix}R'\\R''\end{smallmatrix}$ (Ref. 191)

RING FORMATION

Any five- or six-membered ring containing two contiguous nitrogen atoms is likely to be capable of synthesis from hydrazine. This di-acid base, however, sometimes reacts so that the group appearing in the final ring is a single nitrogen atom having an attached amino group, *i.e.* $>N{-}NH_2$. The ring systems that can be so built will now be taken singly, five-membered rings being considered first.

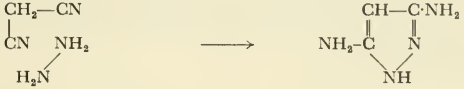
PYRAZOLS

The founder member, pyrazol itself, is best made by adding propargyl aldehyde to a cold solution of hydrazine sulphate in water, allowing the mixture to stand and later heating at 100°C for two hours.[77]



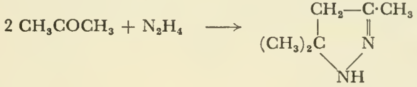
(m.p. 68°C; b.p. 185°C)

Amino groups may be introduced by allowing malonitrile to react with hydrazine hydrate.[78]



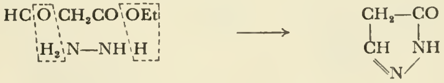
3 : 5-Diaminopyrazol

This ring system, but containing only one double bond (known as a pyrazol*ine*), may be built up when a ketone condenses with hydrazine in strongly acid solution, *e.g.*

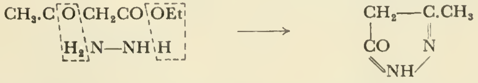


3 : 5 : 5-Trimethyl pyrazoline[79]

The pyrazol*one* ring may be built up by condensation between β-ketoesters and hydrazine, thus:



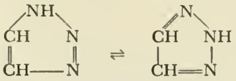
Pyrazolone-5 [80]



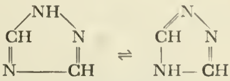
3-Methyl-pyrazolone-5 [80]

TRIAZOLS

Two forms of the triazol ring can exist, known as 1 : 2 : 3- and 1 : 2 : 4-forms; these are shown below, with an indication of the tautomerism of each.

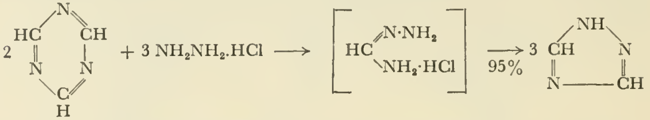


1 : 2 : 3-Triazol
(m.p. 23°C; b.p. 204°C)



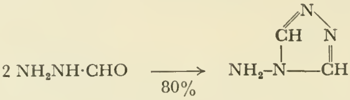
1 : 2 : 4-Triazol
(m.p. 121°C; b.p. 260°C)

Grundmann and Rätz have just published a remarkable synthesis of 1:2:4-triazol itself, which involves refluxing sym-triazine with hydrazine monohydrochloride in alcohol for eight hours.[82]

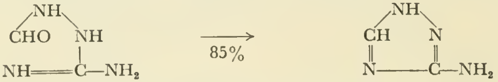


When hydrazine is replaced by methylhydrazine and phenylhydrazine, better than 80 per cent yields of 1-methyl- and 1-phenyl-1:2:4-triazol are obtained, respectively.

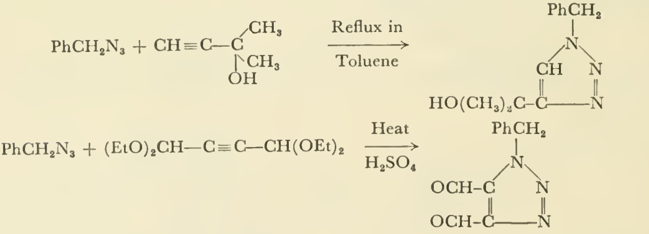
The compound 4-amino-1:2:4-triazol, having the tautomeric formula, may be made by heating formylhydrazine at 150° to 200°C for three hours.[83]



On the other hand, 3-amino-1:2:4-triazol is made by heating an aqueous solution of formyl aminoguanidine on steam.[84]



Derivatives of 1:2:3-triazol, of which many are now known, are made by the action of azides on acetylene derivatives, as illustrated below.



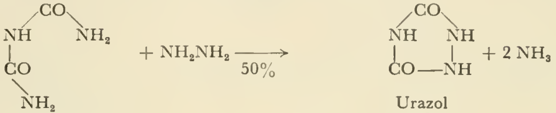
1-Benzyl-1:2:3-triazol-4:5-dialdehyde

The compounds 1:2:3-triazol and 4-formyl triazol have been synthesised from acetylene and propargylaldehyde, respectively, with hydrazoic acid.[85]

URAZOLS

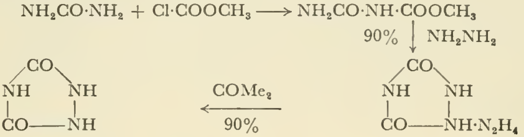
Although listed separately the urazols are really derivatives of triazol, being 1:2:4-triazolidine-diones.

Urazol was originally made by Stollé (1913) by refluxing biuret (1 mol.) with hydrazine hydrate (4 mol.) for three hours. After removing most of the excess hydrazine by vacuum distillation, the remainder is eliminated by shaking with benzaldehyde to precipitate benzalazine, which is filtered off. The remaining benzaldehyde is then extracted with ether, when evaporation of the liquor gives urazol itself.[86]



Urazol
(m.p. 250°C)

Audrieth (1954) condensed allophanic ester with aqueous hydrazine to give the hydrazine salt of urazol, the hydrazine being subsequently removed by refluxing with acetone to form the azine.[87]

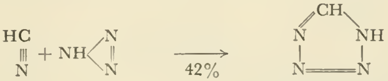


If aqueous hydrazine (13 per cent) be replaced by methanolic hydrazine in the above reaction there is a good yield of aminobiuret.[87]

$$NH_2CO{\cdot}NH{\cdot}COOCH_3 + NH_2NH_2 \xrightarrow{\text{MeOH}} NH_2CO{\cdot}NH{\cdot}CO{\cdot}NH{\cdot}NH_2 + CH_3OH$$

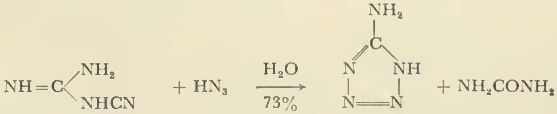
TETRAZOLS

Tetrazols are invariably obtained by the reaction of nitriles with sodium azide, but since the latter can readily be made from hydrazine we are justified in including them here. Acid conditions (acetic acid or dilute mineral acid) are normally used. Tetrazol itself is formed by the reaction between sodium cyanide, sodium azide and acetic acid in *iso*-propanol as solvent under pressure at 110°C for 96 hours.[88]

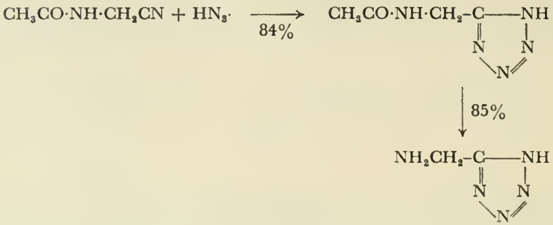


Tetrazol (m.p. 158°C)

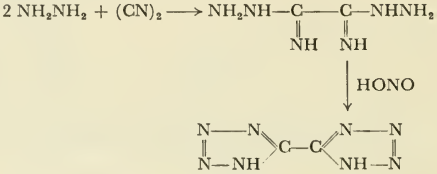
When an equivalent of hydrochloric acid is slowly added to dicyandiamide and sodium azide in water at 65°, 5-aminotetrazol separates.[89]



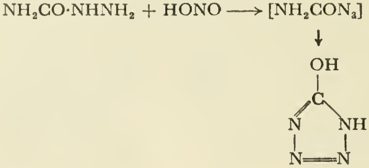
The reaction between aceturic nitrile and sodium azide (3·3 mol.) in tetrahydrofuran with $AlCl_3$ catalyst gives 5-acetaminomethyl tetrazol, which is hydrolysed by concentrated hydrochloric acid under reflux to 5-aminomethyl tetrazol.[90]



Hydrazine condenses readily with cyanogen in cold aqueous solution to give oxalhydrazidine, which reacts with nitrous acid to give bis-tetrazol, a compound which explodes on heating to its melting point.[91]

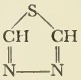


Treatment of semicarbazide with nitrous acid gives 5-hydroxytetrazol.[92]

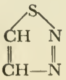


THIODIAZOLS

Two distinct ring systems are known as thiodiazols, which are differentiated as shown below.



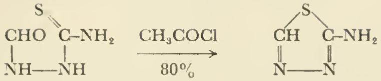
1:3:4-Thiodiazol



1:2:3:-Thiodiazol

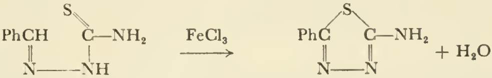
It will be seen that the first is of azine type and the second of azo type.

The 1:3:4-thiodiazols are invariably prepared from substituted thiosemicarbazides or thiosemicarbazones by dehydration and oxidation respectively. Thus formylthiosemicarbazide on dehydration with acetyl chloride gives 2-amino-1:3:4-thiodiazol,[93] from which 1:3:4-thiodiazol (b.p. 121°C) may be made via the 2-bromo compound.

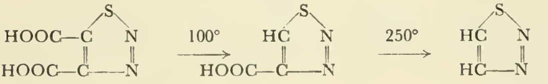


(m.p. 190°C)

The second method of synthesis is illustrated by the ferric oxidation of benzal thiosemicarbazone to give 2-amino-5-phenyl-1 : 3 : 4-thiodiazol.[94]



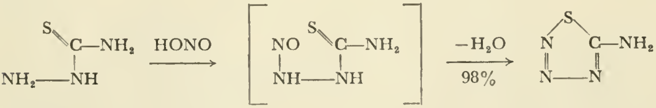
The 1 : 2 : 3-thiodiazols have usually been made from diazoacetic ester, an intermediate that *can* be made from hydrazinoacetic ester, but which would on all normal occasions be made from glycine ester hydrochloride and sodium nitrite. This ring system is of interest, since its heat stability is such that the 4 : 5-dicarboxylic acid may be successively degraded to the parent compound.[95]



(b.p. 158°C)

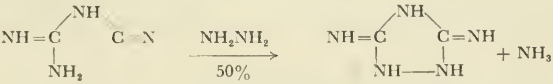
THIOTRIAZOLS

Representatives of this ring system may be made by the action of nitrous acid on substituted thiosemicarbazides. With thiosemicarbazide itself the thermally unstable 2-amino-1 : 3 : 4 : 5-thiotriazole is produced.[96,189]



GUANAZOLS

A separate heading has been given to these compounds although, like the urazols, they are in fact derivatives of 1 : 2 : 4-triazols. Guanazol is best made by the Stollé procedure of heating dicyandiamide with hydrazine hydrate (2·5 mol.) under reflux at 65° to 70°C for some hours, during which ammonia is evolved.[97]

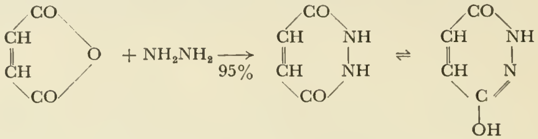


Guanazol
(m.p. 204°C)

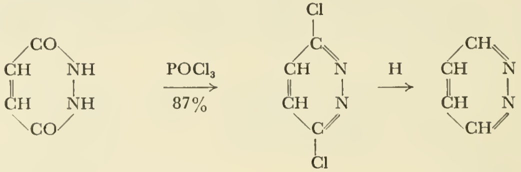
If the temperature of 70°C is exceeded during the reflux period, significant amounts of carbazide and semicarbazide are also produced.

PYRIDAZINES

These are the first of the six-membered rings to be considered. Hydrazine hydrate reacts readily with maleic anhydride in the presence of acid catalysts to give cyclic maleic hydrazide, more correctly termed 1 : 2 : 3 : 4-tetrahydro-pyridazine-1 : 4-dione.[98]

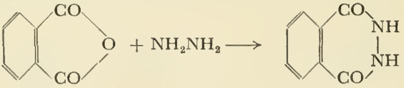


Notwithstanding the fact that cyclic maleic hydrazide shows only mono-enolisation, it reacts with $POCl_3$ to give 3 : 6-dichloropyridazine,[99] which may be reduced to the parent compound.



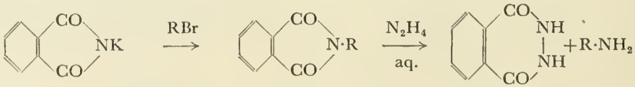
Pyridazine
(b.p. 208°C)

The product obtained when phthalic anhydride is condensed with hydrazine is a benz-maleic hydrazide, but it can also be regarded as a phthalazine derivative.



1 : 2 : 3 : 4-Tetrahydrophthalazine-1 : 4-dione

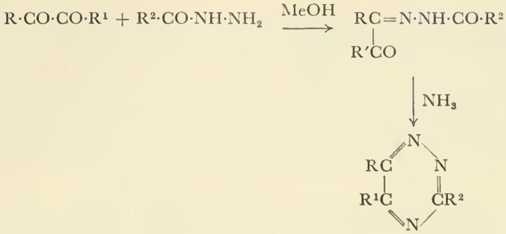
This substance, which is extremely insoluble in water, is a by-product in the modern Gabriel reaction technique where the intermediate phthaloyl compound is hydrolysed by heating with hydrazine hydrate in place of the caustic alkali formerly used.[100]



Owing to enolisation, this by-product is soluble in aqueous bases.

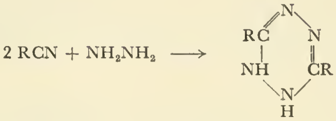
TRIAZINES

The 1 : 2 : 4-triazines may be synthesised by condensation of α-diketones with an acid hydrazide followed by treatment with ammonia at 150°C under pressure.[101]



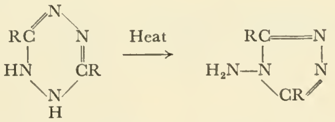
TETRAZINES

Nitriles, when heated with *anhydrous* hydrazine for several days, form substituted tetrazines.[102]



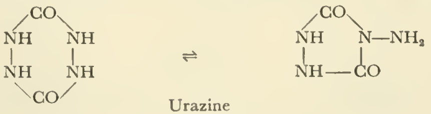
The compound shown is a 3:6-disubstituted-1:2-dihydro-1:2:4:5-tetrazine; tetrazine itself is a red solid of m.p. 99°C.

Substituted 1:2-dihydro-1:2:4:5-tetrazines can readily contract to five-membered rings, forming triazols.



When *aqueous* hydrazine is used in the nitrile condensation, the triazol is indeed the main product.

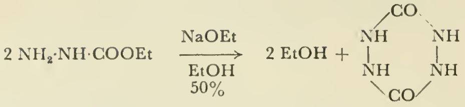
The urazines, which are derivatives of tetrazine, have some importance. They are hexahydrotetrazinediones and tautomerise to five-membered ring compounds,



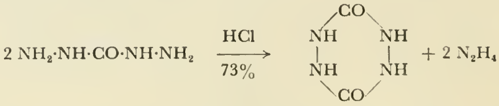
Urazine
(m.p. 275°C)

shown by the fact that shaking with benzaldehyde readily produces 4-benzalaminourazol, the tautomeric form of urazine being 4-aminourazol.[103]

Urazine is a weak *acid* in spite of its tautomerism and forms insoluble silver and barium salts. It is most conveniently prepared by an intermolecular Claisen condensation of ethyl carbazate (ethyl hydrazine carboxylate),[104]

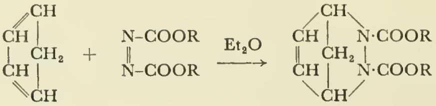


although it may be made by the decomposition of carbazide with strong hydrochloric acid at a temperature rising to 220°C during four hours.[105]

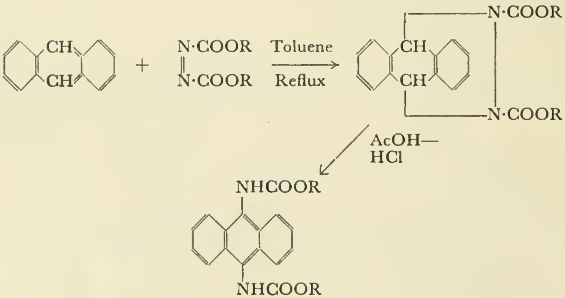


DIELS-ALDER ADDUCTS

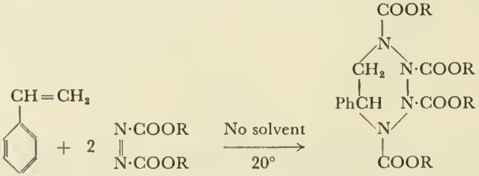
In deriving these adducts from hydrazine-based compounds, we depend on the great facility with which azodicarboxylic esters will add to a conjugated system such as is present in *cyclo*pentadiene, anthracene, styrene or isoprene.



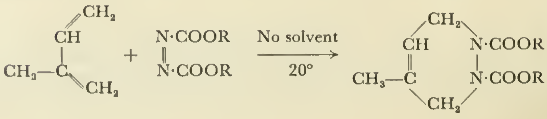
(I)



(II)



(III)



(IV)

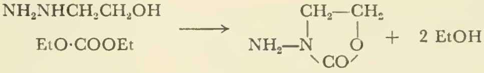
Compounds (I)[106] and (IV)[109] are substituted *pyridazines* or 1:2-diazines and could alternatively have been included under that sub-heading.

Compound (III)[108] is a ring system, a 1:2:3:4-tetrazine, not described elsewhere in this monograph.

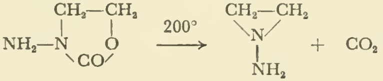
Compound (II)[107] illustrates a very neat way of introducing twin amino groups into the *meso*-positions of anthracene.

MISCELLANEOUS RING SYSTEMS

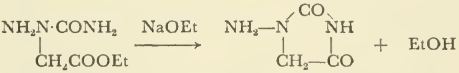
In order to give as nearly complete a picture as possible of the ring systems that hydrazine derivatives can produce, mention should be made of four more examples. When β-hydroxyethyl hydrazine is condensed with ethyl carbonate, an *oxazol* is produced in the form of 3-amino-oxazolidone.



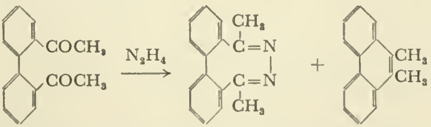
This particular compound is notable in that it decomposes on heating to give *N*-aminoethyleneimine or its polymers.[222]



Amino derivatives of the *imidazol* ring may be synthesised from hydrazine also. Thus the cyclisation of ethyl 2-semicarbazidoacetate gives 1-amino-imidazolidine-2:4-dione.

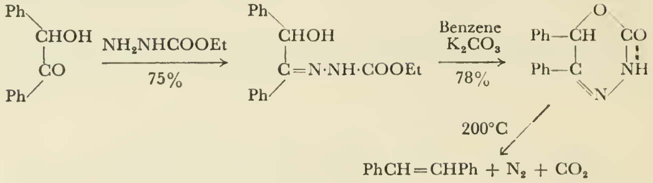


Recently the formation of an eight-membered ring containing contiguous nitrogen atoms has been reported.[110,111] When 2:2′-diacetyl diphenyl reacts with hydrazine, the product is largely (72 per cent) the cyclic azine, a competing reductive cyclisation giving 28 per cent of 9:10-dimethylphenanthrene.



Treatment of diphenyl-2:2′-dialdehyde with hydrazine in hot acetic acid gives a quantitative yield of phenanthrene,[111] showing this reaction to be one of reductive cyclisation only.

Very recently it has been shown[112] that condensation of ethyl hydrazine carboxylate with benzoin first yields the carbethoxyhydrazone, which may then be cyclised to 5:6-diphenyl-2:3-dihydro-1:3:4-oxadiazin-2-one. The latter compound on pyrolysis at 200°C yields nitrogen, carbon dioxide and a mixture of *cis*- and *trans*-stilbene in 75 per cent yield.



III. HYDRAZINE AS A REDUCING AGENT

Hydrazine is a powerful reducing agent which is available commercially both in the anhydrous form and as an aqueous solution of various strengths. In the majority of examples that follow, the reducing agent is used as an aqueous solution, being cheaper and non-hazardous in this form.

Upon decomposition at temperatures above 250°C the products show that at least a second-order reaction is involved, hydrazine in fact being reduced in one of two ways:

$$3N_2H_4 \longrightarrow 4NH_3 + N_2 \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (1)$$

$$2N_2H_4 \longrightarrow 2NH_3 + N_2 + H_2 \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (2)$$

Oxidising agents react with hydrazine to give ammonia, nitrogen and water with or without hydrazoic acid, depending upon the completeness of the reaction. A consideration of the oxidising agents which give (*a*) hydrazoic acid, (*b*) largely nitrogen and ammonia but no hydrazoic acid, and (*c*) only nitrogen, shows that oxidants of varying differences in potential are grouped together. From this result it follows that there is no relationship between the oxidation potential of an oxidant and the nature of the products obtained when hydrazine undergoes oxidation.[114] Were there any such relationship, one would say from the oxidation-reduction potentials given by Latimer[115] (*see* below) that in acid solution hydrazine was stronger in reducing power than tin but weaker than titanous chloride, whereas in alkaline solution it was stronger than sulphite but weaker than hypophosphite.

$$\begin{array}{rcllcr}
Sn^{++} & = & Sn^{++++} + 2e & E^\circ & = & -0{\cdot}15 \\
N_2H_5^{+} & = & N_2 + 5H^{+} + 4e & E^\circ & = & 0{\cdot}23 \\
Ti^{++} & = & Ti^{+++} + e & E^\circ & = & 0{\cdot}37 \\
4OH^{-} + N_2H_4 & = & N_2 + 4H_2O + 4e & E^\circ_B & = & 1{\cdot}17 \\
SO_3^{--} + 2(OH)^{-} & = & SO_4^{--} + H_2O + 2e & E^\circ_B & = & 0{\cdot}93 \\
H_2PO_2^{-} + 3(OH)^{-} & = & HPO_3^{--} + 2H_2O + 2e & E^\circ_B & = & 1{\cdot}57
\end{array}$$

REACTION WITH OXYGEN

Many metals catalyse the oxidation of hydrazine by air to a considerable extent. This catalysis is effective only in alkaline solution.[116,117] Copper and metals that possess more than one valency, and their salts, must be absent or deactivated when hydrazine solutions are distilled. In support of this statement, there are five efficient stabilisers for the protection of hydrazine against aerial oxidation, namely calcium oxide, magnesium oxide, zinc oxide, cadmium oxide and aluminium oxide[118,188]; though all of these compounds are basic, their metals exhibit one valency only. The best general-purpose stabiliser is probably sulphur in minute doses.

The reaction of oxygen with hydrazine is interesting in that hydrogen peroxide is always formed.[120] This fairly rapid reaction, especially effective at higher temperatures, is the basis of the use of aqueous hydrazine solution for the deoxygenation of boiler feed-water.

Reaction with hydrogen peroxide in strongly *acid* solution leads to the formation of hydrazoic acid[121,122,123], (38 per cent of theoretical yield) according to the equation:

$$2N_2H_4 + 2H_2O_2 \longrightarrow HN_3 + NH_3 + 4H_2O$$

The other product of this reaction, ammonia, is produced almost exclusively in *alkaline* solution in the absence of iron and/or copper salts, but in their presence the reaction proceeds largely as follows[124]:

$$N_2H_4 + 2H_2O_2 \longrightarrow N_2 + 4H_2O$$

The reaction of hydrazine with hydrogen peroxide was used in the second world war to provide the motive power of the V-2 rockets. The addition of a small amount of 8-hydroxyquinoline inhibits this extremely vigorous reaction, but when this substance was tried as a reaction modifier in the Raschig synthesis of hydrazine it showed almost no effect.

REACTION WITH NITRITES

Although sodium azide is normally made from sodamide and nitrous oxide, an alternative method involves the reaction of ethyl or butyl nitrite in alkaline alcoholic solution with hydrazine hydrate,[66]

$$C_4H_9ONO + N_2H_4 + NaOH \longrightarrow NaN_3 + C_4H_9OH + 2H_2O$$

when yields exceeding 80 per cent of theoretical may be obtained. Similarly, the azides of potassium, rubidium and caesium may be prepared, these compounds being of special interest, since they decompose at high temperatures to give the pure metal and very pure nitrogen.[125,126]

OXIDATION WITH HALOGENS

Free halogens in acid solution react with hydrazine as follows:

$$2X_2 + N_2H_4 \longrightarrow N_2 + 4HX$$

where X = halogen.[228,229]

This reaction is being used for the purification of crude hydrochloric,[127] hydrobromic and hydriodic acids by removal of excess chlorine, bromine and iodine respectively. To avoid unnecessary dilution of the acid under treatment, the corresponding halogen acid salts of hydrazine may be used.

The reaction with iodine in sodium bicarbonate solution has been used for the estimation of hydrazine; although Vogel[128] postulates the reaction as:

$$5\,N_2H_4 + 2\,I_2 \longrightarrow 4\,N_2H_4{\cdot}HI + N_2$$

the oxidation was previously shown by Kolthoff[129] to proceed as expected, thus:

$$N_2H_4 + 2\,I_2 \longrightarrow 4\,HI + N_2$$

The end-point is fugitive, however, and better results are given by operating in an inert atmosphere such as nitrogen. In the Andrews method, which is the preferred method of hydrazine estimation, iodate is used.

Reaction with hypochlorite can proceed in one of three ways,[195] depending on which reactant is present in excess. Thus, in the presence of excess hydrazine, 3 mol. of N_2H_4 react with 4 mol. NaOCl, the suggested equation being:

$$3\,N_2H_4 + 4\,NaOCl \longrightarrow N_2 + NH_3 + HN_3 + 4\,H_2O + 4\,NaCl$$

With neither in excess, both reactants are destroyed, which suggests the equation:

$$2\,N_2H_4 + 2\,NaOCl \longrightarrow NH_3 + HN_3 + 2\,H_2O + 2\,NaCl$$

When hypochlorite is in excess, 1 mol. N_2H_4 reacts with 2 mol. hypochlorite, suggesting the equation:

$$N_2H_4 + 2\,NaOCl \longrightarrow N_2 + 2\,H_2O + 2\,NaCl$$

Hydrazine reacts quantitatively with sodium chlorite in neutral solution:

$$N_2H_4 + NaClO_2 \longrightarrow N_2 + NaCl + 2H_2O$$

This reaction proceeds more slowly in alkaline solution but can be catalysed by copper or iron salts.[130]

Reaction with bromate and iodate can be made to proceed rapidly with ease to give bromide and iodide, with liberation of nitrogen. This is the basis of the well-known Andrews method[131,132] previously referred to as a method of estimating hydrazine, although in this case the reaction is performed in the presence of 3–5N hydrochloric acid. The equation is:

$$N_2H_4 + KIO_3 + 2HCl \longrightarrow KCl + ICl + N_2 + 3H_2O$$

the primary reaction being one of reduction of iodate to iodide, the latter reacting with more iodate to give iodine monochloride under these conditions.

In the absence of hydrochloric acid, it is possible to halt the reduction at the iodide stage, and this procedure has been used industrially for the conversion of rubidium and caesium bromides to the respective iodides. By treatment of the bromide with iodic acid solution the insoluble iodate is precipitated and the pure compound obtained by evaporation to dryness:

$$6\,RbBr + 7\,HIO_3 \longrightarrow 6RbIO_3 + HI + 3Br_2 + 3H_2O$$

This reaction is quantitative. The residual iodate is then suspended in hot water and a small amount of acetic acid is added, followed by a small portion of 40 per cent hydrazine solution. The mixture is stirred and heated on a steam-bath until the evolution of nitrogen ceases, and the rest of the hydrazine solution needed for complete reduction is added slowly together with a little more acetic acid if necessary. The reaction is complete when addition of more hydrazine and/or acetic acid produces no iodine colour. Evaporation to dryness then leaves pure iodide, this reaction also being quantitative according to the equation:

$$2\,RbIO_3 + 3N_2H_4 \longrightarrow 2\,RbI + 3N_2 + 6H_2O$$

It is interesting to note that Baxter and Tilley[133] found hydrazine hydrate superior to any other reducing agent for the reduction of iodic acid to hydriodic acid in their classical work on the atomic weights of silver and iodine.

Sodium periodate is reduced by hydrazine in acid solution to give iodine but no hydrazoic acid. When separation of iodine is prohibited by the presence of silver sulphate some ammonia and hydrazoic acid are formed.[134]

OXIDATION WITH NITRIC AND NITROUS ACIDS

Concentrated nitric acid reacts with hydrazine sulphate to give some hydrazoic acid,[135] but in the presence of concentrated sulphuric acid nitrogen oxides are evolved.[136] This reaction may be used to remove nitrate from commercial sulphuric acid.

$$2N_2H_4 + 2HNO_3 \longrightarrow 5H_2O + N_2O + 2N_2$$
$$N_2H_4 + 2HNO_3 \longrightarrow 3H_2O + 2NO + N_2O$$

Whereas sodium nitrite and hydrazine salts in the presence of silver nitrate form azides, the reaction between hydrazine sulphate and sodium nitrite alone is represented by:

$$N_2H_4{\cdot}H_2SO_4 + 2NaNO_2 \longrightarrow H_2N_2O_2 + Na_2SO_4 + N_2 + 2H_2O$$

indicating the formation of hyponitrous acid.[137]

MISCELLANEOUS REDUCTIONS

Permanganates in weakly acid solution oxidise hydrazine according to the following equation[129,138]:

$$17N_2H_4{\cdot}H_2SO_4 + 13\,O \longrightarrow 13H_2O + 7(NH_4)_2SO_4 + 10\,N_2 + 10H_2SO_4$$

In more strongly acid solution some hydrazoic acid is also formed.[134]

Trivalent arsenic is not reduced by hydrazine; the pentavalent metal, however, in acid solution and in the presence of potassium bromide, is reduced to As_2O_3, which may be separated by steam-distillation and titrated with bromate in the usual way.[139]

$$2H_3AsO_4 + N_2H_4 \xrightarrow{(HBr)} 2H_3AsO_3 + N_2 + 2H_2O$$

Dichromates are reduced to trivalent chromium in acid solution, the hydrazine appearing mainly as nitrogen.[137] Hexavalent molybdenum is reduced to the pentavalent state in strongly acid solution,[140] though hexavalent tungsten is only partially attacked.

Cerous salts are rapidly formed from ceric with hydrazine in acid solution,[141,122] which will also reduce pentavalent vanadium to the tetra- or tri-valent state depending upon the acidity.[143]

Treatment with hydrazine in acid solution readily reduces ferric[144,145,146] and cobaltic[147] salts to the divalent state. It has been demonstrated[148] that hydrazine sulphate will not readily reduce a suspension of ferric hydroxide of pH 5–7 even upon boiling. However, either hydrazine sulphate or hydrazine hydrate in the presence of the disodium salt of ethylenediamine tetra-acetic acid will convert the suspension at *ca* pH 7 into a clear solution by firstly reducing the ferric ion and secondly by chelating the ferrous ion so formed. Tetravalent lead in both acid and alkaline solutions[149,150] is also reduced to the divalent state

PRODUCTION OF FINELY-DIVIDED METALS

COPPER

The addition of a hot solution of hydrazine sulphate to a suspension of cupric hydroxide in caustic soda results in the complete precipitation of the copper as metal,[151] a reaction not shared by zinc, arsenic and tin.[152] Copper plating may be achieved by a slight modification to this procedure.[153]

SILVER

Silver salts are reduced in alkaline solution to give metallic silver:

$$4AgNO_3 + N_2H_4 + 4NaOH \longrightarrow 4Ag + N_2 + 4NaNO_3 + 4H_2O$$

This deposition is catalysed by colloidal silver and also markedly by copper, or indeed copper salts in solution. James[154] found that as little as five parts of copper per million of solution was sufficient to induce deposition of silver from a solution containing silver nitrate, sodium sulphite and hydrazine that had previously remained stable for several minutes.

When a dilute hydrazine sulphate solution is added slowly to a very dilute alkaline silver solution a stable colloid can be produced.[155]

GOLD

Gold chloride, $AuCl_3$, is completely reduced to the metal in acid, neutral, ammoniacal or alkaline solution,[156] and with very dilute solutions variously coloured colloids may be obtained.[157]

MERCURY

Hydrazine may be used to prepare mercury in powder form,[158] as for example when a solution of a mercuric or mercurous salt containing a little nitric acid is treated with 2 per cent hydrazine solution.[159]

$$2HgCl_2 + N_2H_4 \longrightarrow 2Hg + N_2 + 4HCl$$

NICKEL

The very slow reduction of nickel salts by hydrazine may be speeded enormously by the addition of traces of platinum or palladium salts to alkaline tartrate or ammoniacal solutions.[160]

Salts such as nickel borate are reduced by hydrazine in the presence of palladium, platinum or platinic chloride.[161] A nickel mirror may be similarly deposited upon glass[162] or plastic materials.

PLATINUM METALS

The reduction of platinic chloride in *acid* solution is quantitative and may be written:

$$N_2H_4 + 2PtCl_4 \longrightarrow 2PtCl_2 + 4HCl + N_2$$

In neutral solution the reduction proceeds to metallic platinum, whilst in ammoniacal or acetic acid solution only partial reduction to the metal occurs after long heating.[163] In alkaline solution both K_2PtCl_6 and K_2PdCl_6 are reduced to the metal.[164]

Rhodium salts[165] and osmates[166] are completely reduced to the metals in alkaline solution.

SELENIUM AND TELLURIUM

Selenites are quantitatively reduced to selenium in weak hydrochloric or nitric acid but not in alkaline solutions. Tellurites are not so reduced in the presence of nitric acid, and a possible separation of the two elements has been based on this.[167]

Both selenates and tellurates are rapidly reduced by hydrazine to the elements in weakly acid solution.

APPLICATIONS IN ORGANIC CHEMISTRY

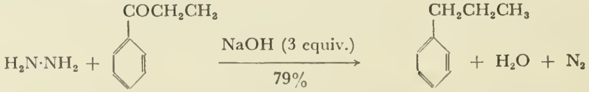
REDUCTION OF CARBONYL COMPOUNDS

Of the three common procedures for the conversion of carbonyl compounds to hydrocarbons—Clemmensen reduction, Kishner-Wolff reduction with hydrazine in the presence of a base, and catalytic hydrogenation—the hydrazine method gives better yields than the first and requires no special equipment. The Kishner-Wolff method cannot be used with compounds that are sensitive to alkali or contain other functional groups that react with hydrazine. It is a particularly useful method of reduction for carbonyl compounds that are sensitive to acids.

It has long been known[142,168,169] that hydrazones of aldehydes and ketones are decomposed by heating with alkali to give the corresponding hydrocarbons and nitrogen gas:

$$RR^1C{=}N{\cdot}NH_2 \xrightarrow{\text{base}} RCH_2R^1 + N_2$$

The method has been improved by the modifications[56] introduced by Huang-Minlon, which enable the reaction to be carried out on a large scale at atmospheric pressure with efficiency and economy. The carbonyl compound is refluxed in a high-boiling water-miscible solvent, usually di- or tri-ethylene glycol, with aqueous hydrazine and sodium or potassium hydroxide to form the hydrazone; water is then allowed to distil from the mixture until the temperature rises to a point favourable for the decomposition of the hydrazone, around 200°C, and the mixture is refluxed for three or four hours to complete the reduction. The reduction of propiophenone to *n*-propylbenzene is a good example of the reaction; yields are usually very satisfactory, those in the aromatic and sterol series being excellent.



A simplified procedure for reducing hydroxy-keto aromatic compounds has been described,[170] as has a modified method for reducing cinnamaldehyde to propenylbenzene in 70 per cent yield.[226]

REDUCTION OF NITRO- AND NITROSO-COMPOUNDS

The use of hydrazine for the reduction of nitro-compounds to amines was first introduced by Curtius. Reduction was generally performed in a sealed tube or autoclave, and it was found with dinitro-compounds that only one of the substituent nitro-groups could be reduced by this means, although, strangely enough, *o*-nitraniline was smoothly converted to *o*-phenylene diamine.[171]

Rothenburg[172] found that hydrazine hydrate could be used at normal pressure in alcoholic solution under reflux, and the reduction of nitrobenzene was described, the equation being:

$$2C_6H_5NO_2 + 3N_2H_4 \longrightarrow 2C_6H_5NH_2 + 4H_2O + 3N_2$$

Here again a fairly recent modification made by Huang-Minlon[173] shows that reduction takes place more readily in diethylene glycol solution under reflux conditions. After a total of three hours reflux *m*- and *p*-toluidines were obtained in yields of 80 and 89 per cent from *m*- and *p*-nitrotoluene respectively. The same products were obtained when the corresponding nitro-aldehydes were similarly treated in the presence of potassium hydroxide, both functional groups having undergone reduction. Unexpected reactions have been known to occur, as for example the reduction of *p*-nitrotoluene in the presence of potassium hydroxide to 4:4′-diaminostilbene. Depending on whether potassium hydroxide was present or absent, reduction of 4:4′-dinitrostilbene gave 4:4′-diaminostilbene or 4:4′-diaminodibenzyl.

Nitroso-compounds were shown[172] to be reduced to the corresponding amines in alcoholic solution under reflux conditions:

$$p\text{-}(CH_3)_2N{\cdot}C_6H_4{\cdot}NO + N_2H_4 \longrightarrow p\text{-}(CH_3)_2N{\cdot}C_6H_4{\cdot}NH_2 + H_2O + N_2$$

although a little diphenylamine also resulted from the reduction of *N*-nitrosodiphenylamine.

REDUCTION OF ACIDS TO ALDEHYDES

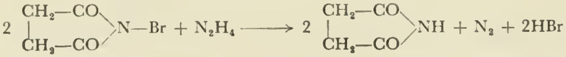
This conversion is accomplished by the reaction of an ester with hydrazine to yield the hydrazide, the benzenesulphonyl derivative of which is then heated with sodium carbonate in aqueous or ethylene glycol solution, the corresponding aldehyde being obtained.[48]

$$ArCOOC_2H_5 \xrightarrow{NH_2NH_2} ArCO{\cdot}NH{\cdot}NH_2 \xrightarrow{C_6H_5SO_2Cl} ArCO{\cdot}NH{\cdot}NH{\cdot}SO_2C_6H_5 \xrightarrow{Na_2CO_3} ArCHO$$

This is the well-known McFadyen and Stevens method for the preparation of aromatic aldehydes; yields can be quite variable.

REDUCTION OF HALOGEN COMPOUNDS

Hydrazine behaves abnormally in dehalogenating chloronitromethanes, α-bromomalonic esters, α-bromo-acetoacetic esters, α-bromobenzoylacetic esters, α-bromo-1:3-diketones and α-bromo-α-nitro fatty acids, with the evolution of nitrogen;[174] *N*-bromosuccinimide is similarly reduced to succinimide.[175]



REDUCTION OF UNSATURATED COMPOUNDS

The hydrogenation of oleic acid by hydrazine hydrate in ethanolic solution has been considered for many years to be a relatively slow reaction. Recent work by Aylward[176] has demonstrated that by using excess hydrazine with good agitation at an elevated temperature as much as 93 per cent of the oleic acid originally present may be converted to stearic acid in six hours. In a like manner elaidic and ricinoleic acids have been hydrogenated with similar success.[177]

Under certain circumstances hydrazine will reduce an azo-group to hydrazo without a catalyst. In this way, short refluxing of ethyl azodicarboxylate with hydrazine hydrate in alcohol leads to an excellent yield of ethyl hydrazodicarboxylate.

CATALYTIC REDUCTIONS WITH HYDRAZINE

PLATINUM AND PALLADIUM CATALYSTS

In 1951, Kuhn[178] reported that the esters of nitric and nitrous acids, and nitro-compounds, are rapidly and quantitatively reduced by hydrazine at room temperature in the presence of a palladium or platinum catalyst according to the equations:

$$2C_6H_{13}ONO_2 + 2N_2H_4 \longrightarrow 2C_6H_{13}OH + N_2O + 3H_2O + 2N_2 \quad .. \quad (3)$$

$$2C_6H_{13}ONO + N_2H_4 \longrightarrow 2C_6H_{13}OH + N_2O + H_2O + N_2 \quad .. \quad (4)$$

$$2C_6H_5NO_2 + 3N_2H_4 \longrightarrow 2C_6H_5NH_2 + 3N_2 + 4H_2O \quad .. \quad .. \quad (5)$$

Excellent yields of hexyl alcohol were obtained in reactions (3) and (4) and of aniline in reaction (5). Similarly, *m*-chloronitrobenzene was quantitatively reduced to the corresponding amine, whereas *m*-dinitrobenzene gave a 75 per cent yield of *m*-nitraniline.

RANEY NICKEL

Two years after Kuhn's report on catalytic reduction, Balcom and Furst[179] in America demonstrated that hydrazine would selectively reduce an aromatic nitro-compound to an amine at temperatures little above normal in the presence of Raney nickel. The reaction, carried out in alcohol, requires only a very small quantity of the catalyst and gives yields of 80 to 99 per cent. Under these conditions carbonyls are unaffected. Among the amines obtained were *p*-aminodiphenyl ether, *p*-aminocinnamic acid and *m*-aminobenzophenone. The method has also been applied[148] to the reduction of 2-methyl-*cyclo*hexanone oxime, which was smoothly converted to the amine in excellent yield.

While the decomposition of hydrazine by platinum black has been shown to occur as follows,[165]

$$3\,N_2H_4 \longrightarrow 4\,NH_3 + N_2$$

decomposition in presence of Raney nickel takes place thus:[180]

$$3\,N_2H_4 \longrightarrow 2NH_3 + 2N_2 + 3H_2$$

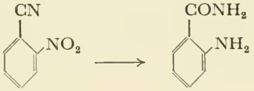
This equation, according to Audrieth,[181] is an over-simplification.

Quite recently it has been reported[182] that aromatic nitriles may be reduced by hydrazine in the presence of Raney nickel to give azines of the corresponding aldehydes:

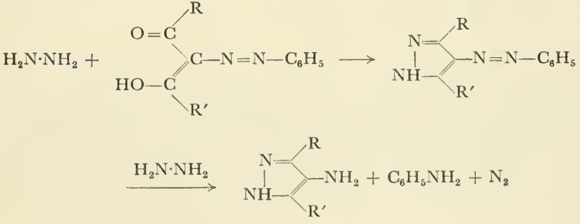
$$2ArCN + 4NH_2NH_2 \longrightarrow 2ArCH{=}N{\cdot}NH_2 \longrightarrow ArCH{=}N{-}N{=}CHAr + N_2H_4$$

Among the compounds that have been reduced in this way are the following: *o*-, *m*- and *p*-methoxybenzonitriles; *o*-, *m*- and *p*-chlorobenzonitriles, and *m*- and *p*-aminobenzonitriles. When *m*- and *p*-nitrobenzonitriles were used, both functional groups underwent reduction to give the same final products, but the yields of the aminoazines were considerably decreased.

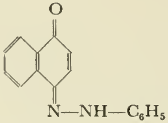
The reduction of the nitro-group in *o*-nitrobenzonitrile proceeds with difficulty with the usual reagents and gives the aminonitrile in poor yield. However, in a recent synthesis of *o*-aminobenzamide,[183] the reduction was effected in better yield by the use of excess hydrazine hydrate in alcoholic solution in the presence of Raney nickel, when the amide was obtained directly, the elements of water adding across the triple bond of the nitrile group under these conditions.



While studying the formation of phenylazopyrazols by the reaction of hydrazine with phenylazo-derivatives of *β*-dicarbonyl compounds, it was observed[184] that excess hydrazine caused the disappearance of the characteristic yellow colour of the desired products. The isolated products proved to be the two amines formed by reductive fission of the azo-linkage:



It was demonstrated that catalysis was involved and that even a piece of porous tile speeded up the reaction as well as Raney nickel. Closer investigation to explore the generality of the reaction revealed that three distinct classes could be recognised. In the first, reaction ceases at the hydrazo stage. This is true of azobenzene, 2-(*o*-chlorophenylazo)-pyridine and 4:4′-azopyridine. In the second class, reaction causes fission to give the two amines, *e.g.* with phenylazo-pyrazoles and 4-aminoazobenzene. In the third class, although reaction of some kind occurred, no pure product could be isolated. In these cases doubts still exist as to the precise structures of some of the starting materials and of their alternative tautomeric formulations, which would allow reaction with hydrazine in a different manner; for example reaction involving the oxygen atom is possible in the following compound:



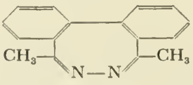
PALLADISED CHARCOAL

Dewar[185] has described the reduction of a wide range of polycylic aromatic nitro-compounds with hydrazine employing the more convenient catalyst, palladised charcoal. Thus 1- and 2-nitro-naphthalenes, 3-nitropyrene, 1-, 2-, 3- and 9-nitrophenanthrene and 3-nitroperylene were all reduced rapidly in at least 60 per cent yield. Nitrobenzene was reduced slowly, but *p*-nitroanisole was converted smoothly to *p*-anisidine, and 8-nitroquinoline gave a good yield of 8-aminoquinoline. The method has also been applied to the reduction of 1:2:6-tribromo-3-nitronaphthalene affording the tribromoamine in 46 per cent yield,[186] whereas no reduction occurred with either the iron powder–ferrous ammonium sulphate method or sodium hyposulphite in alcohol under reflux.

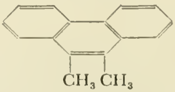
More recently, the catalytic reduction of unsaturated acids to the corresponding saturated compounds with hydrazine and palladised charcoal has been described.[187] For example, maleic and fumaric acids yield succinic acid; crotonic, sorbic and cinnamic acids give butyric, caproic and hydrocinnamic acids respectively. The yields are reported to be in the range 80 to 100 per cent, and the reaction is complete in a few hours at temperatures around 100°C.

REDUCTIVE CYCLISATIONS OF DIALDEHYDES AND DIKETONES

The preparation[110] of the hitherto unknown cyclic azine (I) in 53 per cent yield by the condensation of hydrazine with 2:2′diacetyl diphenyl was accompanied by a reductive cyclisation which yielded about 4 per cent of 9:10-dimethylphenanthrene (II). Some other diketones of this type also gave cyclic azines and dialkylphenanthrenes.



(I)



(II)

Several reductions of this kind have been observed[111] during an investigation into the preparation of cyclic azines containing the unexplored 1:2-diazo*cyclo*octatetraene ring system. Reaction of hydrazine with diphenyl-2:2′dialdehyde yielded no cyclic azine, but nitrogen was evolved and the product was phenanthrene. This reaction occurred very readily at temperatures ranging from 0° to above 100°C, in polar solvents, under acidic or alkaline solutions; in hot acetic acid the yield was quantitative.

Reductions of this type are of practical value in the synthesis of polynuclear compounds; for example, 5:5'dinitro-diphenyl-2:2'-dialdehyde was converted into the previously unknown 3:6-dinitro-phenanthrene; diphenyl-2:2':6:6'-tetra-aldehyde readily gave pyrene. Neither reaction was accompanied by cyclic azine formation.

Ample evidence was obtained to support the conclusion that the phenanthrene compound (II) was not formed by decomposition of the cyclic azine (I).

STABILISATION OF ORGANIC LIQUIDS

Because of its strong reducing power, it is not surprising to find that hydrazine is effective in suppressing the atmospheric oxidation and discoloration of liquid organic compounds such as aromatic amines and monohydric phenols. As little as 0·01 per cent of hydrazine is claimed to prevent the discoloration of aniline.[188]

IV. INDUSTRIAL APPLICATIONS OF HYDRAZINE

BOILER FEED-WATER TREATMENT

The treatment of boiler feed-water in order to remove oxygen and thus reduce or prevent corrosion, is a well-known and established practice. In boilers operating at low pressures this can be adequately and successfully achieved by the use of sodium sulphite, which is converted in the process to sodium sulphate and thus the total dissolved solids content of the water is increased. In boilers operating at high pressures, say at 600 lb/in^2 and above, it is vital to remove oxygen and at the same time preferable to produce no increase in the total dissolved solids content. Hydrazine fulfils this dual role elegantly and successfully, and is thus unique as an oxygen scavenger.[201,202,203]

In this application of hydrazine there are three possible reactions. First, the reaction with oxygen to produce nitrogen and water theoretically needs one pound of hydrazine for one pound of oxygen, but in practice it is advisable to add an appreciable excess. The second is the reaction with ferric oxide, which is reduced to black iron oxide (magnetite). This reaction will use up some excess hydrazine when a system is being treated for the first time, but the reduced film of metallic oxide is then always available to deal with sudden surges of dissolved oxygen. In other words, the film acts as a solid reserve of hydrazine. Thirdly, decomposition of excess hydrazine can occur to produce nitrogen and ammonia, but this is negligible below 350°F.

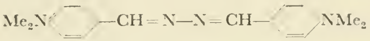
At one time the production of ammonia from hydrazine was felt to militate against its use, for it has always been assumed that ammonia attacks copper alloys. It seems clear, however, that this attack is not caused by ammonia alone, but is more likely due to the combination of ammonia and oxygen. In addition, any carbon dioxide present can be detrimental unless neutralised. A mixture of hydrazine and ammonia, therefore, makes an ideal treatment, as it removes oxygen and keeps the water alkaline. In most instances there is no need to add extra ammonia, as sufficient is formed by decomposition of hydrazine in the steam.

After trials in many parts of the world, the use of hydrazine as an oxygen scavenger in high pressure systems is now well established.[204,205] More recent work has shown that its use in low pressure systems, in marine boilers and in hot-water heating systems is also beneficial and most effective in preventing corrosion.

For these purposes hydrazine is used as a dilute aqueous solution, which is ideal for continuous dosage. Further, in the concentrations normally employed, hydrazine offers no industrial hazard, provided the normal standards of good industrial house-keeping are maintained.

It is used for the protection of idle and stand-by plant. The addition of something like 30 to 50 p.p.m. hydrazine (as N_2H_4), which quantity is normally sufficient to raise the pH substantially above 8·5, has been shown to be of extreme value in protecting idle and stand-by plant against corrosion and maintaining it in a condition that allows it to be put on stream again with the minimum of start-up troubles.

Excess hydrazine is normally measured colorimetrically by formation of the vivid yellow azine with *p*-dimethylamino-benzaldehyde,



although continuous recording electrical meters are now available.[204]

HYDRAZINE AND PLASTICS

A most important and increasingly large outlet for some organic hydrazine derivatives is in the manufacture of blowing agents for the production of expanded plastics and rubber. The physical and chemical properties of those commercially available have been reviewed by Reed.[206] The commercial importance of compounds such as azo-*iso*butyric dinitrile, azo-dicarbonamide, benzene sulphonyl hydrazide and *p,p*′-oxy-*bis*-benzene sulphonyl hydrazide is now well established. All these compounds on decomposition evolve nitrogen, which, under the correct processing conditions, can be used to 'blow' many thermoplastics, such as polyvinyl chloride, polythene and polystyrene. Nylon expansion requires the use of trihydrazinotriazine.[227]

It is important to distinguish between two types of end-product, namely unicellular materials, in which the cell structure is non-interconnecting, and sponge materials, in which some or all of the cells are interconnecting. The production of expanded unicellular P.V.C., a typical plastic of the first type, consists in preparing a suitable mixture of P.V.C., plasticiser, stabiliser and blowing agent, which is fed into a mould and subsequently heated under pressure between the platens of a compression moulding press, when the blowing agent decomposes. As the system is under pressure, gas is unable to escape, and in effect the moulded composition becomes completely filled with minute gas bubbles. After an appropriate heating time the mould and contents are cooled, still under pressure. When cold, the moulding is removed from the press and subsequently expanded in hot water or a suitable hot air oven. In this way it is possible to prepare expanded rigid or highly plasticised P.V.C. with a density as low as 2 lb/cub. ft, and a substantially complete unicellular structure, capable of being formed by heat or vacuum.

The applications of such end-products have yet to be fully exploited, but their importance for marine and buoyancy apparatus, boat building, space filling, cushioning and upholstery is now being fully appreciated and their development is proceeding rapidly.[207]

When sponge materials are required, it is sufficient to carry out the expansion at atmospheric pressure, and processes are now being developed in which a suitably prepared mixture is fed continuously through a tunnel oven in which the appropriate expansion takes place.

In addition, techniques for producing expanded polythene have been developed. Polythene flotation cable, television down-lead cable and so on are commercially produced by extruding, in conventional wire coating apparatus, mixtures of polythene and an appropriate blowing agent, causing the expansion to occur as the coated wire leaves the extruder die.[208]

Blowing agents based on hydrazine also play an important part in the production of expanded rubber, particularly microcellular rubber used for shoe soles. Expanded rubber for many purposes was prepared originally by the use of inorganic blowing agents, such as sodium bicarbonate and ammonium bicarbonate. However, when a unicellular material with a closed cell structure and high abrasion resistance is required as a shoe soling material it is essential to use an organic blowing agent that is to some extent soluble in the rubber and can be completely and thoroughly dispersed through it. Since the war the manufacture of such microcellular rubber has become a substantial industry throughout the world.

For the manufacture of expanded plastics, as much as 30 parts by weight of blowing agent per hundred parts of polymer may be added. Much smaller quantities (say 0·1 to 1·0 per cent on weight of monomer) can be used as polymerisation initiators, as azo compounds are sources of free radicals, the azo link being broken by the action of heat or light. This decomposition occurs smoothly, is seldom affected by the nature of any solvents present and has been shown to be a first order reaction.[209] One of the most commonly used azo initiators is azo-*iso*butyric dinitrile, which is particularly valuable in the polymerisation of methacrylates, acrylonitrile, vinyl acetate and vinyl chloride.[210,211,212] Many other azo compounds have been recommended as initiators,[213] and for methacrylates the methyl and ethyl esters derived from azo-*iso*butyric acid are particularly valuable, even though their large-scale production offers many problems.

As the hydrazine molecule is difunctional, it might well be expected to take part in polycondensation reactions to yield interesting polymers. Certainly, polymeric hydrazides have been prepared,[214] as have polyaminotriazoles.[215] The latter have high melting points and can be drawn as fibres, which from their structure would be expected to dye readily, especially with acid dyes. As yet, however, their manufacture has not been undertaken.

MEDICAL AND BIOLOGICAL APPLICATIONS

Hydrazine perhaps first gained some degree of notoriety through the use of certain hydrazides in the treatment of tuberculosis. The best known is *iso*nicotinic acid hydrazide (I.N.H.), which is manufactured in large quantities throughout the world. It has now been found to be particularly effective when combined with *p*-aminosalicylic acid and streptomycin. In spite of intensive research, it remains unchallenged by any other hydrazide for this particular purpose. More recently, the announcement of the use of cyanacethydrazide for the treatment of husk or lungworm in animals[216] has again pointed to the value of hydrazine derivatives in chemotherapy.

Hydrazine derivatives find outlets in other veterinary applications, particularly for the treatment of coccidiosis. For this purpose two compounds are of special value, firstly the semicarbazone of 5-nitrofurfural and secondly, the product obtained by the condensation of 5-nitrofurfural with *N*-amino oxazolidone, derived from β-hydroxyethyl hydrazine and ethyl carbonate. Both are the subjects of patents by Eaton Laboratories of the U.S.A.

Turning to plant biology, mention must be made of maleic hydrazide, which is now established as a plant-growth regulant. These properties were first reported[217] in 1949 and subsequently developed commercially, initially in the U.S.A.[218]

Maleic hydrazide has since been examined and tested as a plant-growth suppressant for a wide variety of plant species, and copious references to this work exist. In summary, it can be said that its effects are most pronounced on root crops and coarse grasses[219,220] and in preventing the growth of suckers on tobacco plants. Although originally there was some speculation about the toxicity of maleic hydrazide to mammals, this has now been shown to be unfounded,[221] so that its commercial development should now proceed more rapidly.

There are many other smaller outlets for hydrazine derivatives on which it is not proposed to dwell, though mention should be made of the use of hydrazine hydrohalides as soldering fluxes, which decompose completely to leave no corrosive residue. For the soldering of copper in particular, fluxes based on such compounds are highly effective.

This then, is the broad picture of hydrazine and its applications. How the field will alter and expand in the future, it is difficult to predict. It may be confidently expected, however, that the versatility and polyfunctionality of hydrazine and its derivatives will enable them to play an important part in meeting the requirements of new and future technologies.

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